सत्यमेव जयते

INDIAN AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI

I.A.R.I.6.
GIP NLK—H-3 I.A.R.I.—10-5-55—15,000

CANADIAN JOURNAL OF RESEARCH

VOLUME 20
1942
SECTION A

CANADA

Published by the
NATIONAL
RESEARCH COUNCIL
of CANADA

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. JANUARY, 1942 NUMBER 1

ROTATIONAL STRUCTURE OF THE BIRGE-HOPFIELD BANDS OF N_2[1]

BY J. W. T. SPINKS[2]

Abstract

The 2–10, 3–11, 4–12, 5–13, 5–14, and 6–14 bands of the $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ system in N_2 (Birge-Hopfield bands) have been photographed and measured. *P*, *Q*, and *R* branches are recorded and the indentification of the transition as $^1\Pi \rightarrow {}^1\Sigma$ is definitely confirmed. B', B'', α', and α'' values are presented.

Introduction

Molecular nitrogen has a strong system of bands in the Schumann region, and this system has been identified as a $^1\Pi_u - {}^1\Sigma_g^+$ transition (1, 2, 4). Such bands should show *P*, *Q*, and *R* branches, but, so far, measurements of *R* lines have not been recorded and, as a result, the certainty of the assignment of these bands to a $^1\Pi_u - {}^1\Sigma_g^+$ transition has been questioned.

The *P*, *Q*, and *R* branches in question showed up very clearly in some plates of the Birge-Hopfield system taken some time ago, and consequently it was thought worth while to record the results of measurements on these plates.

Experimental

Nitrogen from a cylinder was excited in a discharge tube of the type used for producing an intense hydrogen continuum. The photographs were taken in the third order of the 3-metre grating at the Physikalisches Institute in Darmstadt. Interference by the second order of the strong second positive group of nitrogen was eliminated by a semicylindrical quartz lens mounted in front of the slit of the spectrograph and used as a prism.

Hilger Schumann plates were used.

As usual the spectrum of the iron arc was employed as comparison spectrum and the plates were measured with an Abbé comparator.

Results

Rotational analyses of the 2–10, 3–11, 4–12, 5–13, 5–14, and 6–14 bands have been made. There is a good deal of overlapping in some of the bands, and it is usually impossible to separate the *R* branch lines in the head of the band. As would be expected, the branch lines show alternating intensities. The *Q* branch is much more strongly developed than the *P* and *R* branches, and in most cases was measured to beyond $Q(40)$. Application of combination differences indicates that the Λ doubling in the Π state is very small. Assignments of line frequencies are given in Tables I, II, and III.

---

[1] *Manuscript received October 14, 1941.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

[2] *Professor of Physical Chemistry.*

TABLE I

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	2–10 band. ν_0 = 50,252.50			3–11 band. ν_0 = 49,821.16		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
2	50,250.5	50,244.7$^+$		49,820.4	49,813.6$^+$	49.829.6$^+$
3		39.5$^+$				
4	47.5	35.2$^+$		17.2$^+$	04.2$^+$	32.9$^+$
5	44.7$^+$		50,264.1$^+$			
6	42.0	23.2$^+$	64.1$^+$	11.4	792.7$^+$	32.9$^+$
7	39.5$^+$	16.7	64.1$^+$	08.4$^+$	85.4$^+$	32.9$^+$
8	35.2$^+$	09.6		04.2$^+$		32.9$^+$
9	30.1$^+$	01.9$^+$		00.0	70.8$^+$	
10	25.7	194.5$^+$		795.1	63.4$^+$	29.6$^+$
11	20.5	86.6$^+$		89.7	55.9$^+$	27.1
12	14.7	77.6$^+$	55.7	83.8	47.5$^+$	24.6
13		67.3	51.8	77.9		
14	01.9$^+$	57.6	48.8	70.8$^+$	27.5	17.2$^+$
15	194.5$^+$	46.7	44.7$^+$	63.4$^+$	16.9	13.6$^+$
16	86.6$^+$	36.2		55.9$^+$	06.4	08.4$^+$
17	77.6$^+$	24.9	35.2$^+$	47.5$^+$	695.4	04.2$^+$
18	69.7	13.1	30.1$^+$	39.2	83.4	797.6
19		00.5	23.2$^+$	29.9		92.7$^+$
20	50.8	87.9		20.1	58.0	85.4$^+$
21	40.8	74.2		10.0	45.0	77.9
22	30.1	60.9		699.4	31.2	70.8$^+$
23	19.2	46.8		88.1		63.4$^+$
24	07.5	32.0	186.6$^+$	76.7	02.8	53.9
25	95.5		77.7$^+$	64.4	587.3	47.5$^+$
26	82.7	01.2		51.9	71.8	35.5
27	69.3			38.8	56.0	25.4
28	56.3	49,968.6		25.5	38.9	13.9
29	42.3	51.0		11.2	22.0	03.2
30	27.8			597.1	04.5	692.4

$^+$ *Refers to lines that are overlapped.*

TABLE II

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	4–12 band. ν_0 = 49,391.50			5–13 band. ν_0 = 48,964.05		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
2	49,390.1$^+$	49,383.8$^+$	49,398.5$^+$	48,962.6$^+$	48,956.5$^+$	48,970.7$^+$
3	88.2				52.1	
4	86.6$^+$	74.1$^+$	401.1$^+$	59.0$^+$	46.6$^+$	
5	83.8$^+$	69.2$^+$		56.5$^+$	41.7$^+$	75.1$^+$
6	80.8	62.6	02.8	53.9$^+$	35.4	75.1$^+$
7	77.8$^+$			49.8$^+$		
8	74.1$^+$	47.5$^+$	01.1$^+$	46.6$^+$	22.3	
9	69.2$^+$	40.8$^+$		41.7$^+$	14.7	
10	64.8	33.5$^+$	398.5$^+$	37.3	07.0	70.7$^+$

TABLE II—*Concluded*

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \leftarrow X^1\Sigma_g^+$ N_2 BANDS—*Concluded*

	4–12 band. v_0 = 49,391.50			5–13 band. v_0 = 48.964.05		
	Q)J)	P(J)	R(J)	Q(J)	P(J)	R(J)
11	49,359.7	49,325.8$^+$	49,396.1	48,932.1$^+$	48,898.3$^+$	48,968.0
12	53.9$^+$	17.2$^+$	93.2	26.3$^+$	90.0$^+$	65.6
13	47.5$^+$	08.6$^+$	90.1$^+$	19.8	81.2$^+$	62.6$^+$
14	40.8$^+$	297.5	86.6$^+$	13.1	70.8	59.0$^+$
15	33.5$^+$	86.3	83.8$^+$	05.7	59.9	53.9$^+$
16	25.8$^+$	76.1	77.8$^+$	898.3$^+$	49.6	49.8$^+$
17	17.2$^{\pm}$	65.6		90.0$^+$	38.3	43.9
18	08.6$^+$	53.8	66.8	81.2$^+$	26.9	38.7
19	299.6	41.2		72.2	14.5	32.1$^+$
20	89.9	28.5	53.9$^+$	62.4	01.8	26.3$^+$
21	79.8	14.7	44.8	52.1	788.5	17.8
22	68.9	01.6	39.2	41.7	75.3	11.3
23	58.0	188.1	32.2	30.4	60.8	02.9
24	46.5	73.0	22.6	19.0	46.2	894.2
25	34.0	57.3		06.8	31.1	84.3
26	22.1	42.5	04.3	794.2	15.7	75.7
27				81.3	699.5	65.5
28				67.9	83.2	54.7
29				53.4	66.4	43.7
30				39.3	48.4	32.3

TABLE III

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	5–14 band. ν_0 = 47,009.30			6–14 band. ν_0 = 48,537.5		
	Q(J)	P(J)	R(J)	Q(J)	P(J)	R(J)
0						48,541.7
1						44.2
2	47,008.1$^+$	47,002.6$^+$		48,536.1		46.0
3						
4	04.7$^+$	46,993.4				
5	02.6$^+$	87.6	47,021.1$^+$	30.8		49.2$^+$
6	00.2$^+$	81.9		27.7		49.2$^+$
7	46,997.1	74.7$^+$	21.1$^+$	24.6		
8	93.4	69.2$^+$		20.8	48,496.8	
9	89.0	62.6$^+$		16.0	89.3	
10	84.9$^+$	54.2	18.2	11.8	81.4	
11	79.5$^+$	46.6	16.0	06.3		
12	74.7$^+$	38.2	13.9	00.5		39.9
13	69.2	29.4	11.2	494.1		
14	62.6$^+$	20.2	08.1$^+$	87.5		
15	55.7	10.3	04.7$^+$	80.2		
15	48.9	00.2	00.2$^+$	72.7		
17	41.1	46,889.4	46,995.4	64.5		
18	33.3	78.7	90.4	55.3		
19	24.6	66.9	84.9$^+$	46.0		
20	15.7	55.1	79.5$^+$	37.2	48,377.0	
21	06.4	43.2	72.7	25.0		
22	896.6	29.9	66.1	15.2		
23	86.2	17.0	58.6			
24	75.6	02.8	50.9			
25	64.1	788.5				
26	52.7	73.8	34.0			

TABLE IV

COMBINATION DIFFERENCES, $\Delta_1 F'(J)$, $v' = 5$ (UPPER STATE)

J	$Q(J+1) - P(J+1)$		$R(J) - Q(J)$	
	5–13 band	5–14 band	5–13 band	5–14 band
3	12.4$^+$	11.3$^+$		
4	14.8$^+$	15.0$^+$		
5	18.5$^+$	18.3$^+$	18.7$^+$	
6		22.4$^+$		
7	24.3$^+$	24.2$^+$		
8	26.9$^+$	26.3$^+$		
9	30.3	30.7$^+$		
10	33.9$^+$	32.9$^+$	33.4$^+$	33.2$^+$
11	36.3$^+$	36.5$^+$	35.9$^+$	36.4$^+$
12	38.6$^+$	39.7$^+$	39.3$^+$	39.2$^+$
13	42.3	42.5$^+$	42.8$^+$	42.0$^+$
14	45.9	45.4	45.9$^+$	45.4$^+$
15	48.6$^+$	48.7	48.2$^+$	49.0$^+$
16	51.7$^+$	51.6	51.5$^+$	51.4$^+$
17	54.3$^+$	54.5	53.9$^+$	54.4
18	57.8	57.7	57.5$^+$	57.2
19	60.6	60.5	59.9$^+$	60.3$^+$
20	63.6	63.2	63.9$^+$	62.8$^+$
21	66.4	66.7	65.7	66.3
22	69.5	69.2	69.6	69.6
23	72.9	72.8	72.6	72.4
24	75.7	75.6	75.2	75.2
25	78.5	78.9	77.5	
26	81.8	81.5	81.5	81.3
27	84.7	84.1	84.1	
28	87.0	87.0	86.8	

$^+$ *Using lines that overlap.*

The numbering was determined by the usual methods (see, for example, (3)). Table IV gives combination differences for the 5–13 and 5–14 bands. The agreement of the $\Delta_1 F'(J)$ values indicates that the two bands have the same upper state. The fulfilment of the relation $Q(J+1) - P(J+1) = R(J) - Q(J)$ is illustrated in Table IV for the 5–13 and 5–14 bands and gives a check on the analysis of the bands. The rotational constants B_v were obtained from the combination differences in the usual manner, using Q–P differences. The rotational constant, D, was calculated from the equations below, using preliminary B's.

$$D_v = D_e + \beta(v + \tfrac{1}{2}) : \quad D_e = \frac{-4B_e^3}{\omega_e^2}$$

$$\beta = \frac{\alpha^2}{6\omega_e} + D_e\left(\frac{8\omega_e X_e}{\omega_e} - \frac{5\alpha}{B_e}\right)$$

$$\omega_e'' = 2359.60 : \quad \omega_e' = 1692.28$$

$$\omega_e X_e'' = 14.45 : \quad \omega_e X_e' = 13.32$$

$$D_e' = -6.208 \times 10^{-6} : \quad \beta' = 9.54 \times 10^{-8}$$

$$D_e'' = -5.820 \times 10^{-6} : \quad \beta'' = 0.362 \times 10^{-8}$$

TABLE V

ROTATIONAL CONSTANTS

Band	Upper state, $a^1\Pi_u$		Lower state, $X^1\Sigma_g^+$	
	B'_v, cm.$^{-1}$	D'_v, cm.$^{-1}$(calc.)	B''_v, cm.$^{-1}$	D''_v, cm.$^{-1}$(calc.)
2–10	1.579	-5.97×10^{-6}	1.821	-5.78×10^{-6}
3–11	1.551	-5.87×10^{-6}	1.790	-5.78×10^{-6}
4–12	1.538	-5.78×10^{-6}	1.780	-5.78×10^{-6}
5–13	1.521	-5.68×10^{-6}	1.758	-5.77×10^{-6}
5–14	1.522	-5.68×10^{-6}	1.744	-5.77×10^{-6}
6–14	1.507	-5.58×10^{-6}	1.737	-5.77×10^{-6}

The B values are presented graphically in Fig. 1. The results of Appleyard and of Watson and Koontz (taken from their graph) are included. From the figure, $\alpha' = 0.022$ and $\alpha'' = 0.018$. The large number of R branch lines measured confirms the identification of the system as $a^1\Pi_u \rightarrow X^1\Sigma_g^+$.

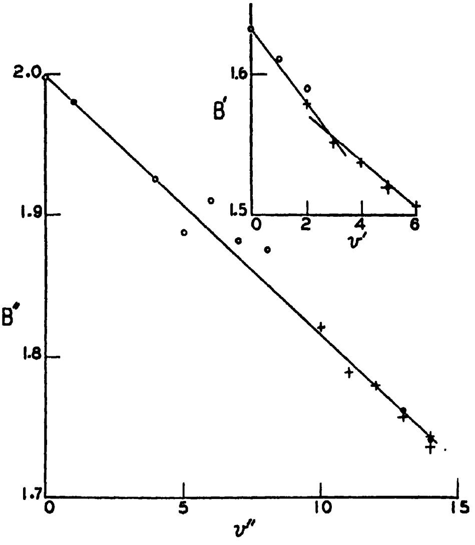


FIG. 1. *B_v vs. v curves for $a^1\Pi_u$ and $X^1\Sigma_g^+$ states of N_2: +, the writer's data; ●, Appleyard's data;* ○, *data of Watson and Koontz.*

Acknowledgments

Gratitude is here expressed to Dr. G. Herzberg, who suggested the problem, and to Dr. Rau of the Physikalische Institut, Darmstadt, who provided facilities for the work.

References

1. APPLEYARD, E. T. S. Phys. Rev. (Ser. 2) 41(2) : 254-255. 1932.
2. BIRGE, R. T. and HOPFIELD, J. J. Astrophys. J. 68 : 257-278. 1928.
3. HERZBERG, G. Molecular spectra and molecular structure. Prentice-Hall, Inc., New York 1939.
4. WATSON, W. W. and KOONTZ, P. G. Phys. Rev. (Ser. 2) 46(1) : 32-37. 1934.

THE VARIANCES OF THE MEANS AND THE VARIANCE OF THE SLOPE OF THE LINE OF RELATION OF A LINEAR, COMPOSITE, BIVARIATE DISTRIBUTION[1]

By F. Charnley[2]

Abstract

The variances of the means and the variance of the slope of the line of relation of a linear, composite, bivariate distribution, in which the variances and correlation coefficient of the component populations remain constant, are analogous to the corresponding variances of a linear regression line. The variances of the means are respectively, $\frac{\sigma_x^2}{N}$, $\frac{\sigma_y^2}{N}$, and the variance of the slope of the line of relation is $\frac{S_{YL}^2}{N(S_X^2 - \sigma_x^2)}$, where σ_x^2, σ_y^2 are the variances of the component populations, S_{YL}^2 is the vertical variance of the composite distribution around the line of relation, N is the total number of measures, and S_X^2 is the variance of the composite distribution around the Y-axis.

The variances of the means and the variance of the slope, m, of the line of relation of a linear, composite, bivariate distribution (1) that are needed in testing the significance of the differences in two lines of relation are entirely analogous to those of the corresponding parameters in a linear regression equation. In view of this close similarity the required variances might therefore be written down by inspection. They are, however, very easily deduced as follows.

Variances of Means

To find the variance in the mean, M_Y, of the composite distribution we need consider only the vertical deviations in the individual means of the component populations. The variance in the mean of a sample of n drawn from a single component population is $\frac{\sigma_y^2}{n}$. Hence, if there are k component populations and a sample of n is drawn from each component, the variance in the mean of the means of the samples will be

$$\frac{k\sigma_y^2}{k^2 n} = \frac{\sigma_y^2}{kn}.$$

If the n's differ, the variance will be

$$\sigma_y^2 \frac{\sum_1^k n_i}{\left(\sum_1^k n_i\right)^2} = \frac{\sigma_y^2}{\sum_1^k n_i}.$$

---

[1] *Manuscript received September 25, 1941.*

Contribution from the Canned Salmon Inspection Laboratory, Department of Fisheries, Vancouver, B.C.

[2] *Chief Chemist.*

Accordingly, in terms of single measures the variance in the mean of the Y-variate of a linear, composite, bivariate distribution is $\frac{\sigma_y^2}{N}$, where $nk = \Sigma n_i = N =$ the total number of measures. And similarly, the variance in the mean of the X-variate is $\frac{\sigma_x^2}{N}$.

Variance of Slope of Line of Relation

From the equation giving the value of m we have

$$m = \frac{\lambda'}{\lambda},$$

where λ' and λ are the respective standard deviations of the means around the means of the composite distribution. If δm is an error in m, then

$$\begin{aligned}\delta m &= \frac{\partial m}{\partial \lambda'}\,\delta\lambda' + \frac{\partial m}{\partial \lambda}\,\delta\lambda \\ &= \frac{\delta\lambda'}{\lambda} - \frac{\lambda'}{\lambda^2}\,\delta\lambda \\ &= \frac{1}{\lambda}(\delta\lambda' - m\delta\lambda).\end{aligned}$$

The square of the error in m is therefore

$$(\delta m)^2 = \frac{1}{\lambda^2}\left[(\delta\lambda')^2 - 2m\delta\lambda\delta\lambda' + m^2(\delta\lambda)^2\right].$$

Summing all the errors and dividing by the number of errors we thus obtain

$$\sigma_m^2 = \frac{1}{\lambda^2}\left[\sigma_{\lambda'}^2 - 2mr\sigma_\lambda\sigma_{\lambda'} + m^2\sigma_\lambda^2\right],$$

in which r is the correlation between the errors in λ and λ'.

Suppose now we draw samples of n from one population. We obtain means $y_{i1}, y_{i2}, \ldots . y_{ij}, \ldots$ These have errors $d_{i1}, d_{i2}, \ldots d_{ij}$. If y_i is the true mean of this population, the squares of the means of the samples are: $y_{i1}^2 = (y_i + d_{i1})^2$, $y_{i2}^2 = (y_i + d_{i2})^2 \ldots .$ The errors in the squares are therefore

$$\begin{aligned}\delta y_{i1}^2 &= y_{i1}^2 - y_i^2 = 2y_i d_{i1} + d_{i1}^2 \\ \delta y_{i2}^2 &= y_{i2}^2 - y_i^2 = 2y_i d_{i2} + d_{i2}^2, \text{ etc.}\end{aligned}$$

If $d_{i1}, d_{i2}, \ldots d_{ij} \ldots$, are small relative to the mean, y_i, which will be true if large samples of n are drawn from this population, $d_{i1}^2, d_{i2}^2, \ldots .$ may be neglected in comparison with $2y_i d_{i1}, 2y_i d_{i2}, \ldots .$ Accordingly, the variance of the square of the average of a sample of n is

$$\overline{(\delta y_i^2)^2} = 4y_i^2\bar{d}_i^2 = 4y_i^2\frac{\sigma_y^2}{n}.$$

But λ'^2 is the mean of the squares of k averages, each squared average having the variance $4y_i^2\frac{\sigma_y^2}{n}$, if the samples drawn from the individual populations are each of size *n*. Hence, the variance of the sum of the squared averages is $4\sum_{1}^{k} y_i^2 \frac{\sigma_y^2}{n}$ and that of the mean of the squared averages

$$4\Sigma y_i^2 \frac{\sigma_y^2}{nk^2} = 4\frac{\sigma_y^2}{nk}\lambda'^2 = \sigma^2_{\lambda'^2}.$$

To find the variance of λ' from this last equation we note that

$$\delta\lambda'^2 = \frac{d\lambda'^2}{d\lambda'}\delta\lambda' = 2\lambda'\delta\lambda'$$

and, consequently,

$$\overline{(\delta\lambda'^2)^2} = 4\lambda'^2\overline{(\delta\lambda')^2} = \sigma^2_{\lambda'^2} = \frac{4\sigma_y^2}{nk}\lambda'^2,$$

giving

$$\overline{(\delta\lambda')^2} = \sigma^2_{\lambda'} = \frac{\sigma_y^2}{nk}.$$

The variances of λ' and λ, the standard deviations of the different means around the means of the composite distribution, are thus merely the variances of the individual means divided by the number of component populations. Furthermore, since the correlation between averages of samples of *n* drawn from a single population is the same as the correlation between single measures (Appendix), the correlation between the errors in λ and λ' must also be *r*, the correlation between single measures in the individual populations. The required variance of *m*, the slope of the line of relation, is accordingly,

$$\sigma_m^2 = \frac{\sigma_y^2 - 2mr\sigma_x\sigma_y + m^2\sigma_x^2}{nk(S_X^2 - \sigma_x^2)}$$

or

$$\sigma_m^2 = \frac{S_Y^2 - 2mp_{XY} + m^2S_X^2}{N(S_X^2 - \sigma_x^2)},$$

in which S_X^2, S_Y^2 are the respective variances of the two variates of the composite distribution around the means of these variates, and *N* is the total number of measures.

The form of the last equation shows that the variance of *m* is a quadratic function of *m*, that it is independent of the nature of the point set representing the means of the component distributions, and that it is applicable to any linear, composite, bivariate distribution. The preceding equation, on the other hand, shows that the equation giving the variance of the slope of a linear regression line (2) is merely the special case of this equation obtained on writing $\sigma_x = 0$.

References

1. Charnley, F. Can. J. Research, A, 19(12) : 139–151. 1941.
2. Fisher, R. A. Statistical methods for research workers. 5th ed. rev. and enl. Oliver and Boyd, Edinburgh. 1934.

APPENDIX

Let samples of n be drawn from a bivariate population in which two characters X and Y are correlated with correlation r. If averages of the two variates in samples of n are correlated, the means of the two distributions will evidently remain the same. Let deviations be taken from the respective means and let

$$u_1 = \frac{x_{11} + x_{12} + - - + x_{1n}}{n}, \quad v_1 = \frac{y_{11} + y_{12} + - - - + y_{1n}}{n}$$

$$- -$$

$$u_N = \frac{x_{N1} + x_{N2} + - - - - + x_{Nn}}{n}, \quad v_N = \frac{y_{N1} + y_{N2} + - - - + y_{Nn}}{n}.$$

Then $\sigma_u = \frac{\sigma_1}{\sqrt{n}}$, $\sigma_v = \frac{\sigma_2}{\sqrt{n}}$, and $\bar{r} = \frac{\Sigma uv}{N\sigma_u\sigma_v}$, where $\bar{r}$ is the correlation between the averages in the samples of n.

Substituting the values of u and v in the product term we have

$$\begin{aligned} \Sigma uv &= u_1v_1 + u_2v_2 + - - - - - + u_Nv_N. \\ n^2\Sigma uv &= (x_{11} + x_{12} + - - - - + x_{1n})(y_{11} + y_{12} + - - - - + y_{1n}) \\ &\quad + (x_{21} + x_{22} + - - - - + x_{2n})(y_{21} + y_{22} + - - - - + y_{2n}) \\ &\quad + - \\ &= x_{11}y_{11} + x_{12}y_{12} + - - - - + x_{1n}y_{1n} + x_{21}y_{21} + x_{22}y_{22} \\ &\quad + - - - - - - - - + x_{2n}y_{2n} + - - - - + \end{aligned}$$

products in which the independent variate of a given pair in a sample is associated with the dependent variates of other pairs in the sample. By a slight extension of the product theorem* the sum of the latter must be zero. Hence

$$n^2\Sigma uv = \Sigma xy,$$

where x and y are corresponding values in single samples. Accordingly,

$$\bar{r} = \frac{\Sigma xy}{n^2}\,\frac{n}{N\sigma_1\sigma_2} = \frac{\Sigma xy}{Nn\sigma_1\sigma_2} = r,$$

since the total number of measures is Nn.

---

*Kelley T. L. Statistical method. The Macmillan Company, New York. 1923.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. FEBRUARY, 1942 NUMBER 2

SECOND GENUS CROSSED ORBITS[1]

BY DANIEL BUCHANAN[2]

Abstract

In a former paper, first genus periodic orbits were obtained for the motion of the electrons in the "crossed orbit" model of the normal helium atom as proposed by Kemble and Bohr. The present paper treats the second genus orbits, i.e., orbits which are in the vicinity of the first genus orbits and which re-enter after the lapse of many first genus periods.

The methods employed involve the solutions of differential equations with periodic coefficients. Notation is introduced which greatly expedites the obtaining of these solutions.

1. Introduction

The problem considered in this paper is to determine second genus periodic orbits for the motion of two infinitesimal bodies that repel each other and are attracted by a third finite body. The forces of attraction and repulsion vary according to the Newtonian law of the inverse square.

As the three bodies in this problem are somewhat analogous to the normal helium atom, the finite body will be referred to as the nucleus and the infinitesimal bodies as the electrons.

2. First Genus Orbits

One periodic orbit is that in which the electrons move in a circle with the nucleus as centre, the electrons remaining diametrically opposite. This plane of motion will be called the *equatorial plane.* Angular distance on either side of it will be called *latitude,* while *longitude* will have the obvious meaning. In a previous paper (2) the author obtained two types of three-dimensional periodic oscillations in the vicinity of this circular orbit. In the first case the longitudes differ by 180°, whereas the latitudes are equal in magnitude but opposite in sign. In the second case the longitudes differ by 180°, but the latitudes are equal in magnitude and also in sign.

The results that were obtained in the paper just cited are similar to those that were first proposed by Kemble and later independently by Bohr for the "Crossed Orbit" model of the normal helium atom (6, Chap. VII).

The present paper treats the second genus orbits for Case I of the author's previous paper cited.

---

[1] *Manuscript received September 13, 1941.*

Contribution from the Faculty of Arts and Science, The University of British Columbia, Vancouver, B.C. Read at the May, 1940, meeting of the Royal Society of Canada.

[2] *Dean.*

3. The Differential Equations

Choose a system of rectangular axes with the nucleus as origin and the equatorial plane as the xy-plane. Let the ratio of repulsion to attraction be denoted by k^2 and let the units of time and of distance be so chosen that the gravitational constant of attraction is unity. If the co-ordinates of the electrons are x_1, y_1, z_1, and x_2, y_2, z_2, the force function is

$$U = \frac{1}{r_1} + \frac{1}{r_2} - \frac{k^2}{r_{12}},$$

$$r_1 = (x_1^2 + y_1^2 + z_1^2)^{1/2}, \qquad r_2 = (x_2^2 + y_2^2 + z_2^2)^{1/2},$$

$$r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2},$$

and the differential equations of motion are

$$\frac{d^2x_j}{dt^2} = \frac{\partial U}{\partial x_j}, \quad \frac{d^2y_j}{dt^2} = \frac{\partial U}{\partial y_j}, \quad \frac{d^2z_j}{dt^2} = \frac{\partial U}{\partial z_j}, \qquad (1)$$

$$j = 1, 2.$$

In Case I of the paper cited above

$$x_2 = -x_1, \quad y_2 = -y_1, \quad z_2 = -z_1. \qquad (2)$$

Then $r_1 = r_2 = \frac{1}{2}r_{12}$. It is then necessary to consider the motion of only one electron, say x_1, y_1, z_1, and the differential equations of its motion are

$$\frac{d^2x_1}{dt^2} = -\frac{\mu x_1}{r_1^3}, \quad \frac{d^2y_1}{dt^2} = -\frac{\mu y_1}{r_1^3}, \quad \frac{d^2z_1}{dt^2} = -\frac{\mu z_1}{r_1^3}, \qquad (3)$$

where $\mu = 1 - \frac{1}{4}k^2$ and $0 < \mu < 1$. Transforming to cylindrical co-ordinates r, θ, z and eliminating $\frac{d\theta}{dt}$ by use of the integral of areas $r^2\frac{d\theta}{dt} = c$, a constant, we obtain the equations

$$\left.\begin{aligned} \frac{d^2r}{dt^2} &= \frac{c^2}{r^3} - \frac{\mu r}{(r^2 + z^2)^{3/2}}, \\ \frac{d^2z}{dt^2} &= \phantom{\frac{c^2}{r^3}} - \frac{\mu z}{(r^2 + z^2)^{3/2}} \end{aligned}\right. \qquad (4)$$

4. The First Genus Orbits

A particular solution of Equations (4) is

$$r = c^2/\mu, \qquad z = 0,$$

being the case in which the electrons move in a circle in the equatorial plane and remain diametrically opposite. To obtain the differential equations of displacement put

$$\left.\begin{aligned} r &= \frac{c^2}{\mu}(1 + \epsilon\rho), \qquad z = \frac{c^2}{\mu}(\epsilon\zeta), \\ t - t_0 &= \frac{c^3}{\mu^2}(1 + \delta)^{1/2}\tau, \end{aligned}\right\} \qquad (5)$$

where ρ, ζ are new dependent variables, τ is the new independent variable, and δ and ϵ are parameters. Thus

$$\begin{aligned}\ddot{\rho} + (1+\delta)\rho &= R = (1+\delta)\left[\epsilon\left(3\rho^2 + \frac{3}{2}\zeta^2\right) - 6\epsilon^2(\rho^3 + \rho\zeta^2)\right.\\ &\qquad \left. + \epsilon^3\left(10\rho^4 + 15\rho^2\zeta^2 - \frac{15}{8}\zeta^4\right) + ---\right],\\ \ddot{\zeta} + (1+\delta)\zeta &= Z = (1+\delta)\left[3\epsilon\rho\zeta - \epsilon^2\left(6\rho^2\zeta - \frac{3}{2}\zeta^3\right) + \epsilon^3\left(10\rho^3\zeta - \frac{15}{2}\rho\zeta^3\right)\right.\\ &\qquad \left. + \epsilon^4\left(-15\rho^4\zeta + \frac{45}{2}\rho^2\zeta^3 - \frac{15}{8}\zeta^5\right) + ---\right],\end{aligned} \tag{6}$$

where the dots denote derivation with respect to τ. The right member R is even in ζ and Z is odd in ζ. In the coefficients of the various powers of ϵ it is found that in R the parity of ρ is opposite that of ϵ, and in Z it is the same as that of ϵ. From these properties it is seen that ρ is odd in ϵ while ζ and δ are both even in ϵ. If the initial values

$$\dot{\rho}(0) = \zeta(0) = 0, \qquad \dot{\zeta}(0) = 1, \tag{7}$$

are taken, the periodic solutions of Equations (6) are

$$\left.\begin{aligned}\rho &= \frac{1}{4}(3 + \cos 2\tau)\epsilon - \frac{1}{64}(51 + 12\cos 2\tau + \cos 4\tau)\epsilon^3 + --,\\ \zeta &= \sin\tau + (0)\epsilon^2 + (0)\epsilon^4 + (\;)\epsilon^6 + --,\\ \delta &= 3\epsilon^2 + (0)\epsilon^4 + (\;)\epsilon^6 + --.\end{aligned}\right\} \tag{8}$$

When these results are substituted in Equations (5) the equations for the periodic orbits of the first genus are obtained.

SECOND GENUS ORBITS

5. Definition

Given a set of differential equations

$$\frac{dx_i}{dt} = X_i(x_j, \epsilon; t), \qquad i, j = 1, ---, n,$$

where the X_i are analytic in the arguments x_j, ϵ and do not contain t explicitly. Suppose they admit the periodic solutions

$$x_i = \theta_i(\epsilon, t)$$

having the period T. These solutions are said to be of the *first genus*. If we substitute

$$\epsilon = \epsilon_0(1 + \lambda), \qquad x_i = \theta_i(\epsilon_0, t) + y_i$$

in the differential equations then solutions for the y_i, say

$$y_i = \Psi_i(\epsilon_0, \lambda; t),$$

can be found having the period

$$NT(1 + \text{a power series in } \lambda),$$

N being an integer. The solutions

$$x_i = \theta_i(\epsilon_0, t) + \Psi_i(\epsilon_0, \lambda; t)$$

are said to be of the *second genus* (5, Vol. 3, Chap. XXVIII). The second genus orbits approach those of the first genus as the parameter λ approaches zero.

6. The Differential Equations

Let $\epsilon = \epsilon_0(1 + \lambda)$, where ϵ occurs explicitly in Equations (6) but not where it enters implicitly through ρ, ζ, and δ. Let ρ_0, ζ_0, δ_0 represent the values in Equations (8) when ϵ is replaced by ϵ_0. Further, let

$$\rho = \rho_0 + p, \qquad \zeta = \zeta_0 + q \tag{9}$$

and let $(1 + \delta)$ be replaced by $(1 + \delta)\,(1 + \gamma)$ where p, q are dependent variables and γ is a parameter that vanishes with λ. The above substitutions will be made in Equations (6) and for the time being the subscript $_0$ on ϵ, δ, ρ, ζ will be dropped. Hence Equations (6) become

$$\begin{aligned} \ddot{\rho} + \ddot{p} + (1 + \delta)(1 + \gamma)(\rho + p) &= (1 + \delta)(1 + \gamma)\Big[3\epsilon(1 + \lambda)\{(\rho + p)^2 \\ &\quad + \tfrac{1}{2}(\zeta + q)^2\} - 6\epsilon^2(1 + \lambda)^2\{(\rho + p)^3 + (\rho + p)(\zeta + q)^2\} + - - -\Big], \\ \ddot{\zeta} + \ddot{q} + (1 + \delta)(1 + \gamma)(\zeta + q) &= (1 + \delta)(1 + \gamma)\Big[3\epsilon(1 + \lambda)(\rho + p) \\ &\quad (\zeta + q) - 3\epsilon^2(1 + \lambda)^2\{2(\rho + p)^2(\zeta + q) - \tfrac{1}{2}(\zeta + q)^3\} + - - -\Big] \end{aligned} \tag{10}$$

where the terms independent of p, q, γ, λ cancel off. When the solutions for ρ, ζ are substituted in the above we obtain

$$\begin{aligned} \ddot{p} + P_{11}p + P_{12}q &= P_1, \\ \ddot{q} + Q_{11}p + Q_{12}q &= Q_1, \end{aligned} \tag{11}$$

where

$$\begin{aligned} P_{11} &= 1 + \frac{3}{2}\,\epsilon^2(1 - 3\cos 2\tau) + \frac{3}{32}\,\epsilon^4(17 + 20\cos 2\tau + 27\cos 4\tau) + - - -, \\ P_{12} &= Q_{11} = -3\epsilon\sin\tau + \frac{3}{8}\,\epsilon^3(11\sin\tau - \sin 3\tau) + - -, \\ Q_{12} &= 1 - \frac{3}{2}\,\epsilon^2(1 - \cos 2\tau) + 3\epsilon^4(1 - \cos 2\tau) + - - -. \end{aligned}$$

The values for P_1, Q_1 will be determined later.

7. The Equations of Variation

If the right members of Equations (11) are neglected,

$$\ddot{p} + P_{11}p + P_{12}q = 0, \qquad \ddot{q} + Q_{11}p + Q_{12}q = 0, \tag{12}$$

and these are called the *equations of variation.* Their *generating solutions* are

$$\begin{aligned} \epsilon\rho &= \frac{1}{4}\epsilon^2(3 + \cos 2\tau) - \frac{1}{64}\epsilon^4(51 + 12\cos 2\tau + \cos 4\tau) + - - -, \\ \epsilon\zeta &= \epsilon\sin\tau + (\quad)\epsilon^6 + - - -. \end{aligned} \tag{13}$$

To obtain the solutions of Equations (12) the usual substitutions

$$p = e^{i\alpha\tau}u, \qquad q = e^{i\alpha\tau}v, \tag{14}$$

are made, where α is a constant and u and v are functions of τ. Equations (12) then become

$$\left.\begin{aligned} (D^2 + 2i\alpha D - \alpha^2 + P_{11})u + P_{12}v &= 0, \\ Q_{11}u + (D^2 + 2i\alpha D - \alpha^2 + Q_{12})v &= 0, \end{aligned}\right\} \tag{15}$$

$$D \equiv \frac{d}{d\tau}.$$

The existence proof, which is omitted here, shows that α, as a power series in ϵ^2, and certain initial values can be determined so that u and v will be periodic with the period 2π.

Now P_{12} and Q_{11} are odd in ϵ while P_{11}, Q_{12} and α are even in ϵ. Then u and v are of opposite parity in ϵ. Since Solutions (14) are later multiplied by arbitrary constants we may for one set of solutions select u as even and v as odd or u as odd and v as even. The former selection will be made and accordingly we assume

$$\left.\begin{aligned} u &= u^{(0)} + u^{(2)}\,\epsilon^2 + u^{(4)}\,\epsilon^4 + - - -, \\ v &= v^{(1)}\,\epsilon + v^{(3)}\,\epsilon^3 + - - -, \\ \alpha &= 1 + \alpha_2\,\epsilon^2 + \alpha_4\,\epsilon^4 + - - -. \end{aligned}\right\} \tag{16}$$

Let Equations (16) be substituted in Equations (15) and let the resulting equations be denoted as (15′). We then equate to zero the coefficients of the various powers of ϵ in (15′) and we thus obtain sets of differential equations that define the various $u^{(2j)}$ and $v^{(2j+1)}$. It will now be shown that the various α_{2j} and certain constants of integration can be determined so that each $u^{(2j)}$ and $v^{(2j+1)}$ will be periodic.

The question of the initial values for u and v will be deferred until after the first step of the integration.

Step 1. Terms in (15′) Independent of ϵ

There is but one differential equation at each step. At this step it is

$$(D^2 + 2iD)u^{(0)} = 0,$$

and its solution is

$$u^{(0)} = A_0 + B_0e^{-2i\tau}.$$

There are two arbitrary constants A_0 and B_0. If we assign the initial value $u(0) = 1$, the solution would be $u^{(0)} = A_0 + (1 - A_0)e^{-2i\tau}$. The integration was carried out with this initial value and the u's and v's were found to contain exponentials having the highest multiples of τ exceeding by two the power of ϵ associated with the u's and v's. This leads to a somewhat complicated form for the final solutions. We therefore choose the initial value $\dot{u}(0) = 0$ from which it follows that each $\dot{u}^{(2j)}(0) = 0$. The desired solution at the first step is then $u^{(0)} = A_0$, where A_0 remains arbitrary.

Step 2. Terms in ϵ

The differential equation is

$$(D^2 + 2iD)v^{(1)} = (3 \sin \tau)u^{(0)},$$

and the solution expressed in terms of exponentials is

$$v^{(1)} = C_1 + D_1e^{-2i\tau} + \frac{iA_0}{2}(e^{i\tau} + 3e^{-i\tau}),$$

where A_0, C_1, D_1 are arbitrary.

Step 3. Terms in ϵ^2

The differential equation is

$$(D^2 + 2iD)u^{(2)} = U^{(2)} = \left(2\alpha_2 - \frac{3}{2} + \frac{9}{2}\cos 2\tau\right)u^{(0)} + (3 \sin \tau)v^{(1)}.$$

Non-periodic terms will arise from the constant terms and terms in $e^{-2i\tau}$ in $U^{(2)}$. These terms are

$$U^{(2)} = 2A_0\alpha_2 + (0)e^{-2i\tau}.$$

Hence either A_0 or α_2 must be zero. To put $A_0 = 0$ would lead to the trivial solution, hence we must put $\alpha_2 = 0$. The integration then yields

$$u^{(2)} = A_2 - \frac{3}{8}A_0(e^{2i\tau} + e^{-2i\tau}) + \frac{i}{2}[C_1e^{i\tau} + 3(C_1 - D_1)e^{-i\tau} + D_1e^{-3i\tau}], \quad (17)$$

where A_0, A_2, C_1, D_1 are arbitrary.

Step 4. Terms in ϵ^3

The differential equation is

$$(D^2 + 2iD)v^{(3)} = V^{(3)} = -\frac{3}{8}(11 \sin \tau - \sin 3\tau)u^{(0)} + (3 \sin \tau)u^{(2)}$$
$$+ \frac{3}{2}(1 - \cos 2\tau)v^{(1)}.$$

Now $V^{(3)}$ contains the terms

$$V^{(3)} = 3\left(C_1 - D_1\right) - \left(3C_1 - \frac{11}{2}D_1\right)e^{-2i\tau}, \quad (18)$$

and these terms must be annulled if $v^{(3)}$ is to be periodic. Hence $C_1 = D_1 = 0$ and $u^{(2)} = A_2 - \frac{3}{8}A_0(e^{2i\tau} + e^{-2i\tau})$. The integration for $v^{(3)}$ will then be

$$v^{(3)} = C_3 + D_3e^{-2i\tau} + \frac{iA_2}{2}(e^{i\tau} + 3e^{-i\tau}) - \frac{iA_0}{8}(3e^{i\tau} - 3e^{-i\tau} - 4e^{-3i\tau}),$$

where A_0, A_2, C_3, D_3 are arbitrary. The constants C_3, D_3 remain arbitrary through Step 5 but at Step 6 they enter $V^{(5)}$ the same as C_1, D_1 occur in Equation (18). Hence $C_3 = D_3 = 0$ and these terms will be ignored in $v^{(3)}$ above.

Step 5. Terms in ϵ^4

The differential equation is

$$(D^2 + 2iD)u^{(4)} = U^{(4)} = 2\alpha_4u^{(0)} - \frac{3}{2}(1 - \cos 2\tau)u^{(2)}$$
$$- \frac{3}{32}(17 + 20 \cos 2\tau + 27 \cos 4\tau)u^{(0)} \quad (19)$$
$$+ (3 \sin \tau)v^{(3)} - \frac{3}{8}(11 \sin \tau - \sin 3\tau)v^{(1)}.$$

So far as the constants and terms in $e^{-2i\tau}$ enter $U^{(4)}$ we have

$$U^{(4)} = A_0\left(2\alpha_4 - \frac{99}{32}\right) - \left(\frac{3}{2}A_2 - \frac{45}{16}A_0\right)e^{-2i\tau}.$$

Hence

$$\alpha_4 = -\frac{99}{64}A_0, \qquad A_2 = \frac{15}{8}A_0,$$

and the desired solution for $u^{(4)}$ is

$$u^{(4)} = A_4 - A_0\left(\frac{335}{256}e^{-2i\tau} + \frac{9}{64}e^{2i\tau} - \frac{93}{1536}e^{4i\tau} - \frac{165}{256}e^{-4i\tau}\right),$$

where A_0, A_4 are arbitrary.

The General Step

At the 7th step, $U^{(6)}$ contains the terms

$$U^{(6)} = A_0(2\alpha_6 + \text{constant}) - \left\{\frac{3}{2}A_4 + A_0\,(\text{constant})\right\} e^{-2i\tau},$$

and there are no other terms where α_6 and A_4 enter. Hence α_6 and A_4 can be uniquely determined. The arbitrary constants arising through a v-equation enter the next v-equation as in Equation (18) and must be annulled. An induction to the general term will readily show that the α's and the constants of integration can be uniquely determined as above. Since A_0 remains arbitrary we may take $A_0 = 1$, as we later multiply u by an arbitrary constant.

One set of solutions of the equations of variation has thus been found, viz.,

$$p = e^{i\alpha\tau}u_1, \qquad q = e^{i\alpha\tau}iv_1, \tag{20}$$

where

$$\begin{aligned} u_1 &= 1 - \frac{3}{4}\,\epsilon^2(\cos 2\tau) + - - - , \\ &= \sum_{j=0}^{\infty}\sum_{k=0}^{j}\,[A_k^{(2j)}\cos 2k\tau + i\,B_k^{(2j)}\sin 2k\tau]\epsilon^{2j}, \\ v_1 &= \epsilon\,(2\cos\tau - i\sin\tau) + (\quad)\epsilon^3 + - - , \\ &= \sum_{j=0}^{\infty}\sum_{k=0}^{j}\,[C_k^{(2j+1)}\cos(2k+1)\,\tau + i\,D_k^{(2j+1)}\sin(2k+1)\tau]\epsilon^{2j+1}, \\ \dot{u}_1(0) &= 0. \end{aligned}$$

A second set of solutions can be obtained by changing the sign of i in Equations (20) thus

$$p = e^{-i\alpha\tau}\,u_2, \qquad q = e^{-i\alpha\tau}\,(-\,iv_2), \tag{21}$$

where

$$u_2 = \bar{u}_1, \qquad v_2 = \bar{v}_1.$$

The remaining two sets of the solutions of the equations of variation can be obtained, as shown by Poincairé (5, Vol. 1, Chap. IV), by partial differentiation of the generating solutions Nos. (13) with respect to the two arbitrary constants that they contain, viz., the initial time t_0 and the scale factor ϵ.

Differentiating Equations (13) first with respect to t_0 we obtain

$$p = \frac{\partial(\epsilon\rho)}{\partial t_0} = -\frac{\mu^2}{c^3}\frac{1}{(1+\delta)^{1/3}}\frac{\partial(\epsilon\rho)}{\partial\tau} = -\frac{\mu^2}{c^3}\frac{1}{(1+\delta)^{1/3}}u_3,$$

where

$$u_3 = -\frac{1}{2}\,(\sin 2\tau)\epsilon^2 + \frac{1}{16}\,(6\sin 2\tau + \sin 4\tau)\epsilon^4 + - - -,$$

$$q = \frac{\partial(\epsilon\zeta)}{\partial t_0} = -\frac{\mu^2}{c^3}\frac{1}{(1+\delta)^{1/3}}\frac{\partial(\epsilon\zeta)}{\partial\tau} = -\frac{\mu^2}{c^3}\frac{1}{(1+\delta)^{1/3}}\,v_3,$$

where

$$v_3 = (\cos\tau)\epsilon + (\quad)\epsilon^7 + - - - .$$

Since these solutions are later multiplied by arbitrary constants, we may drop the constant multipliers of u_3 and v_3 and take

$$p = u_3, \qquad q = v_3 \tag{22}$$

as the solutions.

Differentiating Equations (13) with respect to ϵ we obtain

$$p = \left(\frac{\partial(\epsilon\rho)}{\partial\epsilon}\right) + \frac{\partial(\epsilon\rho)}{\partial\tau}\,\frac{\partial\tau}{\partial\delta}\,\frac{\partial\delta}{\partial\epsilon},$$

$$q = \left(\frac{\partial(\epsilon\zeta)}{\partial\epsilon}\right) + \frac{\partial(\epsilon\zeta)}{\partial\tau}\,\frac{\partial\tau}{\partial\delta}\,\frac{\partial\delta}{\partial\epsilon},$$

where the parentheses about the partial derivatives denote partial differentiation only in so far as ϵ enters ρ and ζ explicitly. Performing the differentiations and multiplying the results by ϵ so as to make the power of ϵ the same as that of the highest multiplicity of τ in its coefficient, we obtain

$$p = u_4 + K\tau u_3\,, \qquad q = v_4 + K\tau v_3\,,$$

$$u_4 = \frac{1}{2}(3 + \cos 2\tau)\epsilon^2 - \frac{1}{16}(51 + 12\cos 2\tau + \cos 4\tau)\epsilon^4 + --,$$

$$v_4 = (\sin\tau)\epsilon + (\quad)\epsilon^7 + --,$$

$$K = -\frac{3}{2}\epsilon^2 + \frac{9}{2}\epsilon^4 + --.$$

The criterion that the four sets of solutions that have been obtained constitute a fundamental set is that the determinant formed from these solutions and their first derivatives must be different from zero. This determinant is

$$\Delta = \left.\begin{array}{llll} u_1 & u_2 & u_3 & u_4 + K\tau u_3 \\ \dot{u}_1 + i\alpha u_1 & \dot{u}_2 - i\alpha u_2 & \dot{u}_3 & \dot{u}_4 + K(\tau\dot{u}_3 + u_3) \\ iv_1 & -iv_2 & v_3 & v_4 + K\tau v_3 \\ i\dot{v}_1 - \alpha v_1 & -i\dot{v}_2 - \alpha v_2 & \dot{v}_3 & \dot{v}_4 + K(\tau\dot{v}_3 + v_3) \end{array}\right| . \tag{23}$$

Since the equations of variation do not contain τ explicitly, this determinant is a constant (4, §18). Its value may be obtained with the minimum of computation by putting $\tau = 0$. We thus obtain

$$\Delta = -2i\epsilon^2\,[1 + \epsilon^2 \text{ (a power series in } \epsilon^2)]\,,$$

and this is different from zero for ϵ not zero but sufficiently small numerically. Hence the four solutions constitute a fundamental set, and the most general solutions of the equations of variation are

$$\begin{aligned} p &= K_1 e^{i\alpha\tau}u_1 + K_2 e^{-i\alpha\tau}u_2 + K_3u_3 + K_4(u_4 + K\tau u_3), \\ q &= i(K_1 e^{i\alpha\tau}v_1 - K_2 e^{-i\alpha\tau}v_2) + K_3v_3 + K_4(v_4 + K\tau v_3)\,, \end{aligned} \tag{24}$$

where K_1, K_2, K_3, K_4 are arbitrary constants.

8. Notation

As we shall have frequent occasions in the sequel to use power series in odd or even powers of ϵ with sums of sines or cosines of odd or even multiples of τ in the coefficients, we shall adopt a notation* that will represent these series and denote their properties.

The letters C and S will denote the power series referred to above, C representing series with cosines in the coefficients and S with sines. Their

---

**This notation was first used by the author in his paper "Periodic orbits of the second genus near the straight line equilibrium points in the problem of three bodies" (1).*

properties will be indicated by superscripts consisting usually of two parentheses. In the first parentheses will appear a digit followed by the letter o or e. The digit will represent the power of the lowest term in ϵ, and the parity of this digit will be the same as that of the parity of ϵ in the series, zero being taken as even. The letters o and e will signify that the multiples of τ in the sines or cosines are odd or even respectively.

The highest multiple of τ in the coefficient of ϵ^j is usually j but occasionally it exceeds j. When it is the same as j no second parenthesis in the superscript will appear. When it exceeds j a second parenthesis will be added containing a digit denoting the excess of the multiple over the power. Thus

$$
\begin{aligned}
C^{(0,e)} &= \sum_{j=0}^{\infty} \sum_{k=0}^{j} (a_{2k}^{(2j)} \cos 2k\tau)\, \epsilon^{2j}, \\
C^{(1,e)(1)} &= \sum_{j=0}^{\infty} \sum_{k=0}^{j+1} (a_{2k}^{(2j+1)} \cos 2k\tau)\, \epsilon^{2j+1}, \\
S^{(0,o)(1)} &= \sum_{j=0}^{\infty} \sum_{k=0}^{j} (b_{2k+1}^{(2j)} \sin (2k+1)\tau)\, \epsilon^{2j}.
\end{aligned}
$$

The symbols C and S with superscripts but without subscripts will denote *types* of series only. When a particular series of a type is to be noted, subscripts will be used.

Expressed in the above notation, the generating solutions and the u's and v's of the equations of variation are represented as follows:

$$
\begin{array}{llll}
\rho = C^{(1,e)(1)}, & & \zeta = S^{(1,o)(1)}, \\
u_1 = C^{(0,e)} + iS^{(0,e)}, & & u_2 = \bar{u}_1, \\
v_1 = C^{(1,o)} + iS^{(1,o)}, & & v_2 = \bar{v}_1, \\
u_3 = S_3^{(2,e)}, & & v_3 = C_3^{(1,o)}, \\
u_4 = C_4^{(2,e)}, & & v_4 = S_4^{(1,o)}.
\end{array}
$$

9. The Highest-Multiple-Power Property

Certain pairs of series like u_3, u_4 have the property that the coefficient of the sine of the highest multiple of τ in the coefficient of any power of ϵ in one series is the same as, or differs only in sign from, the coefficient of the cosine of the highest multiple of τ in the coefficient of the same power of ϵ in the other series. This property will be called the Highest-Multiple-Power property and will be abbreviated to H.-M.-P. The word *same* or *opposite* will follow according as the coefficients in question are of the same or opposite signs, respectively. Thus

u_3, u_4, H.-M.-P. opposite

v_3, v_4, H.-M.-P. same.

10. Construction of the Periodic Solutions

We proceed to show that Equations (10) can be integrated as power series in λ and that γ and the constants of integration can be uniquely determined so that p and q will be periodic with the period T, a multiple of 2π, and will satisfy certain initial conditions.

Let us assume

$$p = \sum_{j=1}^{\infty} p_j \lambda^j, \quad q = \sum_{j=1}^{\infty} q_j \lambda^j, \quad \gamma = \sum_{j=1}^{\infty} \gamma_j \lambda^j, \tag{25}$$

and let these substitutions be made in Equations (10). The resulting equations will be cited as (10′). On equating the coefficients of the various powers of λ in Equations (10′) we obtain sets of differential equations from which the p_j and the q_j will be found. It will be shown that the γ_j and the arbitrary constants arising at each step can be so chosen as to satisfy the periodicity and certain initial conditions.

As the first genus orbits are symmetric, that is, $\dot{\rho}(0) = \zeta(0) = 0$, we shall confine our attention to the symmetric second genus orbits. Hence we put $\dot{p}(0) = q(0) = 0$ and when these conditions are imposed upon Equations (25) we have

$$\dot{p}_j(0) = q_j(0) = 0, \ (j = 1, 2, 3, - - -).$$

It will be found that, under the above initial conditions, one constant of integration will remain arbitrary at each step of the solutions for p_j and q_j. We may therefore impose an additional condition and we shall choose $p(0) = 1$. Hence $p_1(0) = 1$, $p_j(0) = 0, j > 1$. There is no loss of generality here as p carries the factor λ in Equations (25). The parameter λ then becomes the scale factor of the second genus orbits.

Step 1. Coefficients of λ *in Equations (10′)*

On equating the coefficients of λ in Equations (10′) we obtain

$$\begin{aligned} \ddot{p}_1 + P_{11}p_1 + P_{12}q_1 &= P^{(1)} = \gamma_1 C^{(1,e)(1)} + C^{(1,e)(1)}, \\ \ddot{q}_1 + Q_{11}p_1 + Q_{12}q_1 &= Q^{(1)} = \gamma_1 S^{(0,o)(1)} + S^{(2,o)(1)}. \end{aligned} \tag{26}$$

The complementary functions of these equations are

$$\begin{aligned} p_1 &= k_1^{(1)} e^{i\alpha\tau} u_1 + k_2^{(1)} e^{-i\alpha\tau} u_2 + k_3^{(1)} u_3 + k_4^{(1)}(u_4 + K\tau u_3), \\ q_1 &= i(k_1^{(1)} e^{i\alpha\tau} v_1 - k_2^{(1)} e^{-i\alpha\tau} v_2) + k_3^{(1)} v_3 + k_4^{(1)}(v_4 + K\tau v_3), \end{aligned} \tag{27}$$

where $k_1^{(1)}, - - -, k_4^{(1)}$ are the arbitrary constants. By using the method of the variation of parameters to find the particular integrals we have

$$\begin{aligned} &\dot{k}_1^{(1)} e^{i\alpha\tau} u_1 + \dot{k}_2^{(1)} e^{-i\alpha\tau} v_2 + \dot{k}_3^{(1)} u_3 + \dot{k}_4^{(1)}(u_4 + K\tau u_3) = 0, \\ &\dot{k}_1^{(1)} e^{i\alpha\tau}(\dot{u}_1 + i\alpha u_1) + \dot{k}_2^{(1)} e^{-i\alpha\tau}(\dot{u}_2 - i\alpha u_2) \\ &\qquad + \dot{k}_3^{(1)} \dot{u}_3 + \dot{k}_4^{(1)}\{\dot{u}_4 + K(\tau\dot{u}_3 + u_3)\} = P^{(1)}, \\ &\dot{k}_1^{(1)} e^{i\alpha\tau} i v_1 - \dot{k}_2^{(1)} e^{-i\alpha\tau} i v_2 + \dot{k}_3^{(1)} v_3 + \dot{k}_4^{(1)}(v_4 + K\tau v_3) = 0, \\ &\dot{k}_1^{(1)} e^{i\alpha\tau}(i\dot{v}_1 - \alpha v_1) - \dot{k}_2^{(1)} e^{-i\alpha\tau}(i\dot{v}_2 + \alpha v_2) \\ &\qquad + \dot{k}_3^{(1)} \dot{v}_3 + \dot{k}_4^{(1)}\{\dot{v}_4 + K(\tau\dot{v}_3 + v_3)\} = Q^{(1)}. \end{aligned} \tag{28}$$

The determinant of $\dot{k}_1^{(1)}, - - -, \dot{k}_4^{(1)}$ is the same as in Equations (24) and therefore does not vanish for $\epsilon \neq 0$ but small numerically. Equations (28) are therefore solvable, the solutions being

$$\begin{aligned} \Delta\dot{k}_1^{(1)} &= -e^{-i\alpha\tau}(M_{12}P^{(1)} + M_{14}Q^{(1)}), \\ \Delta\dot{k}_2^{(1)} &= e^{i\alpha\tau}(M_{22}P^{(1)} + M_{24}Q^{(1)}), \\ \Delta\dot{k}_3^{(1)} &= -(M_{32}P^{(1)} + M_{34}Q^{(1)}), \\ \Delta\dot{k}_4^{(1)} &= (M_{42}P^{(1)} + M_{44}Q^{(1)}), \end{aligned} \tag{29}$$

where $M_{jk}(j = 1, 2, 3, 4; k = 2, 4)$ are the co-factors of the elements in the determinant Δ, j referring to the column and k to the row. The forms of these co-factors in terms of the notation adopted, together with their properties, are given in Table I.

TABLE I

THE CO-FACTORS AND THEIR PROPERTIES

Co-factors	Type of series	Functions	H.-M.-P. properties
$M_{12} = \overline{M}_{22}$	$\epsilon^2(C_{12}{}^{(0,e)} + iS_{12}{}^{(0,e)})$		
$M_{14} = \overline{M}_{24}$	$i\epsilon^2(C_{14}{}^{(1,o)} + iS_{14}{}^{(1,o)})$		
M_{32}	$i(C_{32}^{(2,e)} + K\tau S_{42}^{(2,e)})$	$C_{32}^{(2,e)}$, $S_{42}^{(2,e)}$	Opposite
M_{42}	$iS_{42}^{(2,e)}$		
M_{34}	$i(S_{34}^{(1,o)} + K\tau C_{44}^{(1,o)})$	$S_{34}^{(1,o)}$, $C_{44}^{(1,o)}$	Same
M_{44}	$iC_{44}^{(1,o)}$		

On making the necessary substitutions in the first two of Equations (29), integrating and substituting the results in Equations (27) we obtain particular integrals for p_1, q_1 which are respectively of the same form as the right members of Equations (26). Non-periodic terms, however, will arise if α is an even integer. Those values of ϵ that will make α an even integer must therefore be excluded.

The integration of the last two of Equations (29) proceeds differently from the preceding integration. When the series involved are expressed in the notation employed,

$$\dot{k}_3^{(1)} = \frac{1}{\epsilon}\gamma_1 d_1^{(1)} + \epsilon d_2^{(1)} + \gamma_1 C_{32}^{(1,e)(3)} + C_{42}^{(1,e)(3)} + K\tau(\gamma_1 S_3^{(1,e)(3)} + S_4^{(1,e)(3)}),$$

$$\dot{k}_4^{(1)} = -\gamma_1 S_{32}^{(1,e)(3)} - S_{42}^{(1,e)(3)} - \gamma_1 S_3^{(1,e)(3)} - S_4^{(1,e)(3)},$$

where

$C_{32}^{(1,e)(3)}$, $S_{32}^{(1,e)(3)}$ have H.-M.-P. opposite,

$C_{42}^{(1,e)(3)}$, $S_{42}^{(1,e)(3)}$ have H.-M.-P. opposite,

and where the $d_j^{(h)}$ here and in the sequel denote power series in ϵ^2 with constant terms different from zero.

When the integrations are performed and the results for $k_3^{(1)}$ and $k_4^{(1)}$ are substituted in Equations (27), the non-periodic terms arising from the integration of $\gamma_1 S_3^{(1,e)(3)} + S_4^{(1,e)(3)}$ in $\dot{k}_3^{(1)}$, $\dot{k}_4^{(1)}$ cancel off and we obtain

$$\begin{aligned} p_1 &= \gamma_1 C^{(3,e)(1)} + C^{(3,e)(1)} + K_3^{(1)} u_3 + \left(KK_4^{(1)} + \frac{1}{\epsilon}\gamma_1 d_1^{(1)} + \epsilon d_2^{(1)}\right)\tau u_3, \\ q_1 &= \gamma_1 S^{(2,o)(1)} + S^{(2,o)(1)} + K_3^{(1)} v_3 + \left(KK_4^{(1)} + \frac{1}{\epsilon}\gamma_1 d_1^{(1)} + \epsilon d_2^{(1)}\right)\tau v_3. \end{aligned} \tag{30}$$

Because of the H.-M.-P. properties listed, the numbers in the second parentheses of the superscripts of C and S are 1 instead of 3.

From the periodicity conditions we must put

$$KK_4^{(1)} + \frac{1}{\epsilon}\gamma_1 d_1^{(1)} + \epsilon d_2^{(1)} = 0, \tag{31}$$

and the complete solutions at the first step become

$$\begin{aligned} p_1 &= K_1^{(1)} e^{i\alpha\tau} u_1 + K_2^{(1)} e^{-i\alpha\tau} u_2 + K_3^{(1)} u_3 + K_4^{(1)} u_4 + \gamma_1 C^{(1,e)(1)} + C^{(1,e)(1)}, \\ q_1 &= i(K_1^{(1)} e^{i\alpha\tau} v_1 - K_2^{(1)} e^{-i\alpha\tau} v_2) + K_3^{(1)} v_3 + K_4^{(1)} v_4 + \gamma_1 S^{(0,o)(1)} + S^{(2,o)(1)}, \end{aligned} \tag{32}$$

where $K_1^{(1)}, ---, K_4^{(1)}$ are the constants of integration. The part of the particular integrals in Equations (30) obtained from the integration of $\dot{k}_3^{(1)}$ and $\dot{k}_4^{(1)}$ have been absorbed by the corresponding particular integrals arising from $\dot{k}_1^{(1)}$ and $\dot{k}_2^{(1)}$.

The period of the above solutions must be a multiple of $2\pi/\alpha$ and also of 2π. Hence α must be rational, i.e., $\alpha = N_1/N$, where N_1 and N are relatively prime integers. The period will then be

$$T = N_1\left(\frac{2\pi}{\alpha}\right) = N(2\pi). \tag{33}$$

From the initial conditions $\dot{p}_1(0) = 0$, or $q_1(0) = 0$, and $p_1(0) = 1$, it follows that

$$K_1^{(1)} = K_2^{(1)} = 1, \qquad K_3^{(1)} = 0.$$

The solutions, therefore, which satisfy the initial and periodicity conditions are

$$\begin{aligned} p_1 &= e^{i\alpha\tau} u_1 + e^{-i\alpha\tau} u_2 + K_4^{(1)} u_4 + \gamma_1 C^{(1,e)(1)} + C^{(1,e)(1)}, \\ q_1 &= i(e^{i\alpha\tau} v_1 - e^{-i\alpha\tau} v_2) + K_4^{(1)} v_4 + \gamma_1 S^{(0,o))} + S^{(2,o)(1)}, \end{aligned} \tag{34}$$

where $K_4^{(1)}$ and γ_1 must satisfy Equation (31).

Step 2. Terms in λ^2

It will be necessary to consider the terms in λ^2 where another relation between $K_4^{(1)}$ and γ_1 will arise which together with Equation (31) will uniquely determine these constants.

The differential equations at this step are

$$\begin{aligned} \ddot{p}_2 + P_{11} p_2 + P_{12} q_2 &= P^{(2)}, \\ \ddot{q}_2 + Q_{11} p_2 + Q_{12} q_2 &= Q^{(2)}, \end{aligned} \tag{35}$$

and the complementary functions are the same as Equations (27) with $k_1^{(2)}, ---, k_4^{(2)}$ as the arbitrary constants. We shall require first only the terms in $e^{\pm i\alpha\tau}$ in the right members. So far as these terms are concerned,

$$\begin{aligned} P^{(2)} &= e^{i\alpha\tau}[\epsilon K_4^{(1)}(C^{(2,e)} + iS^{(2,e)}) + \gamma_1(C^{(0,e)} + iS^{(0,e)}) + C^{(2,e)} + iS^{(2,e)}] \\ &\quad + e^{-i\alpha\tau}[\qquad \text{conjugate} \qquad], \\ Q^{(2)} &= ie^{i\alpha\tau}[\epsilon K_4^{(1)}(C^{(1,o)} + iS^{(1,o)}) + \gamma_1(C^{(1,o)} + iS^{(1,o)}) + C^{(1,o)} + iS^{(1,o)}] \\ &\quad - ie^{-i\alpha\tau}[\qquad \text{conjugate} \qquad]. \end{aligned} \tag{36}$$

In the above and in the sequel the word "conjugate" in the parentheses designates the conjugate of the function in the parenthesis immediately preceding.

On varying the parameters $k_1^{(2)}$, $k_2^{(2)}$ we obtain

$$\begin{aligned} \Delta\dot{k}_1^{(2)} &= -\,e^{-i\alpha\tau}[M_{12}P^{(2)} + M_{14}Q^{(2)}], \\ \Delta\dot{k}_2^{(2)} &= \quad e^{i\alpha\tau}\,[M_{22}P^{(2)} + M_{24}Q^{(2)}]. \end{aligned} \tag{37}$$

When the substitutions are made for the M's, P's, and Q's in Equations (37), constant terms will arise which must be annulled if the solutions at this step are to be periodic. This gives the second relation in $K_4^{(1)}$ and γ_1

$$\epsilon K_4^{(1)} d_1^{(2)} + \frac{1}{\epsilon^2}\,\gamma_1 d_2^{(2)} + d_3^{(2)} = 0, \tag{38}$$

which along with Equation (31) will give

$$K_4^{(1)} = \frac{1}{\epsilon}\,d_4^{(2)}, \qquad \gamma_1 = \epsilon^2 d_5^{(2)}. \tag{39}$$

On substituting Equations (39) in Equations (34) the solutions at the first step take the form

$$\begin{aligned} p_1 &= e^{i\alpha\tau}u_1 + e^{-i\alpha\tau}u_2 + C^{(1,e)(1)}, \\ q_1 &= e^{i\alpha\tau}iv_1 - e^{-i\alpha\tau}iv_2 + S^{(0,o)(2)}. \end{aligned} \tag{40}$$

When we make use of Equations (40) instead of Equations (34), the right members $P^{(2)}$, $Q^{(2)}$ take the form

$$\begin{aligned} P^{(2)} &= \epsilon e^{2i\alpha\tau}(C^{(0,e)} + iS^{(0,e)}) + \epsilon e^{-2i\alpha\tau}\ (\text{conjugate}) \\ &\quad + \epsilon^2 e^{i\alpha\tau}(C^{(0,e)} + iS^{(0,e)}) + \epsilon^2 e^{-i\alpha\tau}\ (\text{conjugate}) \\ &\quad + C^{(1,e)(1)}, \\ Q^{(2)} &= \epsilon e^{2i\alpha\tau}(iC^{(1,o)} + S^{(1,o)}) + \epsilon e^{-2i\alpha\tau}\ (\text{conjugate}) \\ &\quad + e^{i\alpha\tau}(iC^{(1,o)} + S^{(1,o)}) + e^{-i\alpha\tau}(\text{conjugate}) \\ &\quad + S^{(2,o)(1)}. \end{aligned}$$

Varying the parameters $k_3^{(2)}$, $k_4^{(2)}$ we have equations similar to the last two Equations (29), if we replace the superscript (1) with (2). These two equations will give a relation between $K_4^{(2)}$ and γ_2 similar to Equation (31). When the integrations are completed and we impose the further condition $p_2(0) = 0$ we obtain

$$\begin{aligned} p_2 &= \sum_{j=1}^{2} (e^{ij\alpha\tau}\,U_{j1}^{(2)} + e^{-ij\alpha\tau}\,U_{j2}^{(2)}) + C^{(1,e)(1)}, \\ q_2 &= i\sum_{j=1}^{2} (e^{ij\alpha\tau}\,V_{j1}^{(2)} - e^{-ij\alpha\tau}\,V_{j2}^{(2)}) + S^{(2,o)(1)}, \end{aligned}$$

where $U_{j1}^{(k)}$ is similar to u_1, $V_{j1}^{(k)}$ to v_1; $U_{j1}^{(k)}$, $U_{j2}^{(k)}$ are conjugates and so also are $V_{j1}^{(k)}$, $V_{j2}^{(k)}$.

The integration for the higher terms in p and q may be carried on as far as desired. One relation $K_4^{(j)}$ and γ_j will be obtained at the step where $K_4^{(j)}$ arises and a second relation will be found at the next succeeding step. The general form will therefore be

$$\begin{aligned} p_n &= \sum_{j=1}^{n} (e^{ij\alpha\tau}U_{j1}^{(n)} + e^{-ij\alpha\tau}U_{j2}^{(n)}) + C^{(1,e)(1)}, \\ q_n &= i\sum_{j=1}^{n} (e^{ij\alpha\tau}V_{j1}^{(n)} - e^{-ij\alpha\tau}V_{j2}^{(n)}) + S^{(2,o)(1)}, \end{aligned}$$

and the final form for r and z is

$$r = \frac{c^2}{\mu}\left[1 + \epsilon\left(\rho + \sum_{n=1}^{\infty} p_n\lambda^n\right)\right],$$

$$z = \frac{c^2}{\mu}\,\epsilon\left(\zeta + \sum_{n=1}^{\infty} q_n\lambda^n\right).$$

The period in t of the first genus is

$$T_1 = \frac{c^3}{\mu^2}(1 + \delta)^{\frac{1}{2}}\, 2\pi$$

and of the second

$$T = N_1 T_1\left(1 + \sum_{n=1}^{\infty} \gamma_n\lambda^n\right).$$

11. The Convergence of the Solutions

Only the formal construction of the solutions has been made and it now remains to consider their convergence. The usual method of establishing the convergence is by an existence proof based upon Poincaré's extension to Cauchy's theorem (5, Vol. 1, pp. 58-63). Such existence proofs are long and actually more difficult than the formal construction. An alternative method is to make use of MacMillan's theorem (3) where he showed that if the constants of integration can be determined so as to make the solutions of differential equations similar to those arising here *formally* periodic, then such solutions will converge for all finite values of the time, provided the scale factor, such as λ, is sufficiently small numerically.

References

1. Buchanan, D. Proc. Roy. Soc. (London) A, 114 : 490-516. 1927.
2. Buchanan, D. Rend. Circolo Mat. Palermo, 60 : 1-21. 1931.
3. MacMillan, W. D. Trans. Am. Math. Soc. 13 (2) : 146-158. 1913.
4. Moulton, F. R. Periodic orbits. Carnegie Institution, Washington, D.C. 1920.
5. Poincaré, H. Les méthodes nouvelles de la mécanique céleste. Gauthiers-Villars, Paris. 1892–1899.
6. Van Vleck, J. H. Bull. Nat. Research Council. Vol. 10, Pt. 4, No. 54. 1926.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. MARCH, 1942 NUMBER 3

ABSORPTION OF LIGHT AND HEAT RADIATION BY SMALL SPHERICAL PARTICLES

II. SCATTERING OF LIGHT BY SMALL CARBON SPHERES[1]

BY R. RUEDY[2]

Abstract

Spheres of carbon for which $2a/\lambda$, the ratio between the diameter of the particle and the incident wave-length, is less than about $\frac{1}{10}$ scatter the light uniformly in all directions. The intensity of the scattered radiation for any angle is proportional to the square of the volume of the particle and inversely proportional to the fourth power of the wave-length. As the ratio $2a/\lambda$ increases from $\frac{1}{4}$ to $\frac{1}{2}$ and greater values, the diffused light collects more and more into a main beam that appears as a continuation of the incident ray and that decreases in width as $2a/\lambda$ increases. Blue light prevails in the scattered radiation. When the size of the particles is unknown, the intensity, distribution, and polarization of the scattered light give an at least approximate value for the radius.

Amount of Light Scattered by Small Spherical Particles of Carbon

The loss of light observed behind a small spherical obstacle brought into the path of a plane wave of light may be large for two reasons, either because a large portion of the incident light that enters the obstacle is transformed into heat, or because a large portion of the incident light is deflected in other directions by the obstacle. It is to be expected that if the sphere consists of carbon, absorption accounts for the larger part of the loss; indeed, the relatively high index of refraction of carbon indicates that the electrons yield readily to an external alternating field; the conductivity, however, is moderate and the ohmic losses caused by the motion of the electrons are considerable.

In order to determine exactly what fraction of the total loss measured behind a spherical carbon particle is due merely to scattering or diffraction of the light, and what fraction is lost by true absorption, it is necessary to consider both the real and the imaginary part of the amplitudes a_ν and p_ν of the component electric and magnetic waves for which the solution of the problem is obtained. For an incident wave of unit intensity in air these amplitudes are as follows.

---

[1] *Manuscript received November 22, 1941.*

Contribution from the Research Plans and Publications Section, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1032.

Part I, containing the general formulae, appeared in Can. J. Research, 19 (10) : 117-125, 1941.

[2] *Research Investigator.*

$$a_\nu = \frac{(-1)^\nu(2\nu+1)}{-i+(-1)^\nu \dfrac{J_{-\nu-\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} \dfrac{\dfrac{\beta}{\alpha}\dfrac{J'_{-\nu-\frac{1}{2}}(\alpha)}{J_{-\nu-\frac{1}{2}}(\alpha)} - \dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}{\dfrac{\beta}{\alpha}\dfrac{J'_{\nu+\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} - \dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}}$$

$$p_\nu = \frac{(-1)^{\nu+1}(2\nu+1)}{-i+(-1)^\nu \dfrac{J_{-\nu-\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} \dfrac{\dfrac{\beta}{\alpha}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)} - \dfrac{J'_{-\nu-\frac{1}{2}}(\alpha)}{J_{-\nu-\frac{1}{2}}(\alpha)}}{\dfrac{\beta}{\alpha}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)} - \dfrac{J'_{\nu+\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)}}}.$$

In the present instance, when $\alpha = 2\pi a/\lambda$ the derivatives

$$J'_{\nu+\frac{1}{2}}(\alpha) = J_{\nu-\frac{1}{2}}(\alpha) - \frac{\nu}{\alpha} J_{\nu+\frac{1}{2}}(\alpha)$$

$$J'_{-\nu-\frac{1}{2}}(\alpha) = -J_{-\nu+\frac{1}{2}}(\alpha) - \frac{\nu}{\alpha} J_{-\nu-\frac{1}{2}}(\alpha),$$

are approximately equal to the derivatives of the Bessel functions of half-integral order. The real part and the imaginary part of each of the components a_ν and p_ν are entirely different functions of the ratio $2a/\lambda$ or of $\alpha = 2\pi a/\lambda$, as a glance at Figs. 1 to 4 will show. For very small values of α the value of a_ν increases as $\alpha^{2\nu+1}$; that for p_ν increases as $\alpha^{2\nu+3}$. For larger and larger values of α, the rate of increase of a_ν and p_ν diminishes, and after a few fluctuations, a_ν and p_ν vary regularly according to the law

$$a_\nu = \frac{2\nu+1}{n-in\kappa+1} i^\nu(\cos\alpha + i\sin\alpha)\left((n-in\kappa)i\cos\left(\alpha-\nu\frac{\pi}{2}\right) + \sin\left(\alpha-\frac{\nu\pi}{2}\right)\right)$$

$$-p_\nu = \frac{2\nu+1}{n+1-in\kappa} i^\nu(\cos\alpha + i\sin\alpha)\left(i\cos\left(\alpha-\nu\frac{\pi}{2}\right) + (n-in\kappa)\sin\left(\alpha-\frac{\nu\pi}{2}\right)\right).$$

It follows that in this final stage the real parts of a_ν and p_ν oscillate between

$$\pm\frac{2\nu+1}{2}\,\frac{1-n^2-n^2\kappa^2}{(1+n)^2+n^2\kappa^2},$$

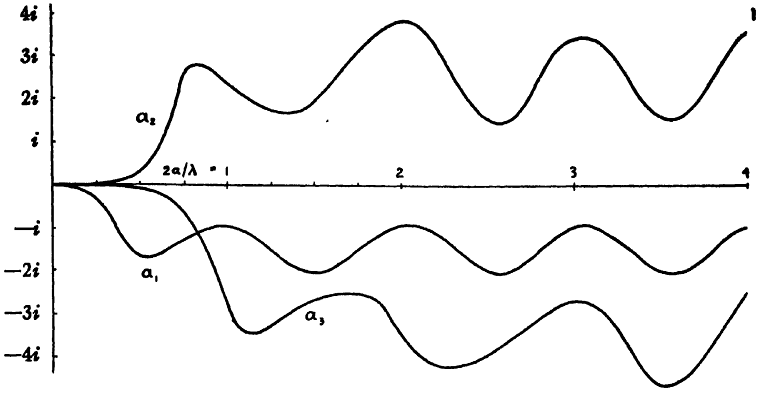
the positive values occurring for multiples of π, the negative for odd multiples of $\pi/2$ when the formula is used for a_ν (Figs. 2 and 4). For surroundings other than air, n has to be divided by the refractive index m_0 of the medium.

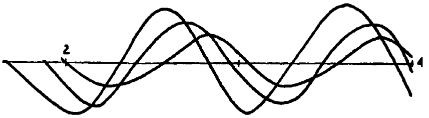
The imaginary portions of a_ν and p_ν, on the other hand, reach much higher values (Figs. 1 and 3); apart from the sign, which remains unchanged, these values alternate regularly between

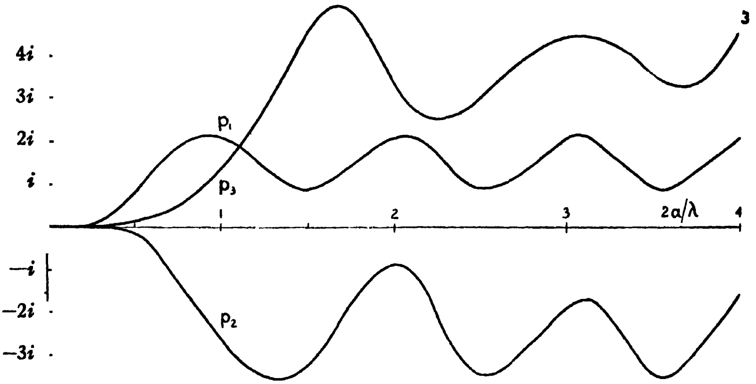
$$(2\nu+1)\frac{1+n}{(1+n)^2+n^2\kappa^2} \text{ and } (2\nu+1)\frac{n^2+n+n^2\kappa^2}{(1+n)^2+n^2\kappa^2}$$

and are thus simply proportional to $(2\nu+1)$.

When, therefore, larger and larger ratios are chosen for α, the imaginary part of the difference $(-1)^\nu(a_\nu - p_\nu)$, which determines the total loss of light along the direction of the incident ray, becomes equal to $i\nu^2$. Calculations show the number ν of components that contribute appreciably to







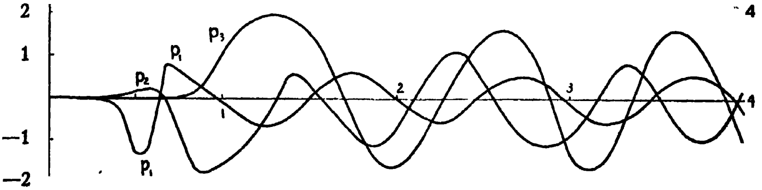


FIG. 1. *Imaginary part of the amplitudes of the electrical component waves set up by spherical carbon particles of different ratios 2a/λ.* FIG. 2. *Real part of the amplitudes of the electrical component waves set up by the particles.* FIG. 3. *Imaginary part of the amplitudes of the magnetic component waves sent out by particles having different ratios 2a/λ.* FIG. 4. *Real part of the amplitudes of the component magnetic waves sent out by carbon particles.*

the sum of all the expressions $(-1)^\nu(a_\nu - p_\nu)$ to be equal to α; there follows the relation

$$\text{imag. part of } \Sigma(-1)^\nu(a_\nu - p_\nu) = \alpha^2 .$$

Hence the actual surface, $2\pi a^2$, that the obstacle presents to the light, and not merely its cross-section, is involved in the absorption and deflection of the wave.

Of the fraction lost per unit length of path,

$$k = \text{imaginary component of } \frac{\lambda^2}{2\pi m_0^2}\Sigma(-1)^\nu(a_\nu - p_\nu),$$

when there is one particle per unit volume, the amount

$$k_s = \frac{\lambda^2}{2\pi m_0^2}\Sigma\frac{|a_\nu|^2 + |p_\nu|^2}{2\nu + 1}$$

is lost as a result of the deflection of the light in other directions. The symbol $|a|$ means the absolute value of the complex quantity a. The values calculated for carbon particles are shown in Fig. 5 for various diameters of the particle ($2a = 0.15, 0.2, 0.3$, and $0.4\ \mu$). They are seen to be small in the visible region at least, and to decrease in general with the wave-length, most steeply when the diameter $2a$ of the particle is in the neighbourhood of 0.3μ; for this size the loss in the visible diminishes markedly as the wave-length is increased.

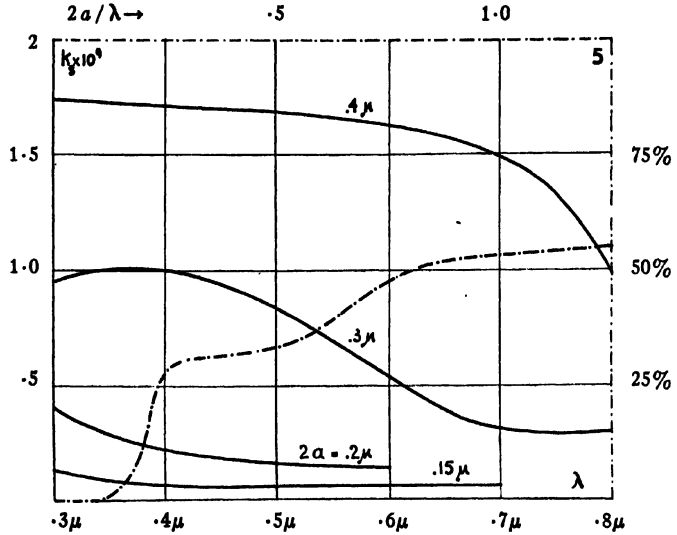


FIG. 5. *Loss of light caused by scattering for one particle per unit volume and percentage of total loss caused by diffusion (dot-dash lines).*

Ratio Between Loss by Deflection and Total Loss

For very small values of α, only one component, the electric wave of amplitude a_1, where

$$a_1 = 2\alpha^3 \frac{(n - in\kappa)^2 - 1}{(n - in\kappa)^2 + 2},$$

need be considered. It follows that the ratio of deflected light to the total fraction of the radiation lost along the direction of the incoming wave, owing to the presence of the particle, is equal to

$$R = 2\alpha^3 \frac{(n^2 - n^2\kappa^2 - 1)(n^2 - n^2\kappa^2 + 2) - i6n\kappa}{(n^2 - n^2\kappa^2 + 2)^2 + 4n^2\kappa^2}.$$

The ratio is zero when the particles are extremely small but increases considerably as values between $\pi/10$ and $\pi/4$ are given to α. For very large values of α the fraction tends towards the limit

$$R_l = \frac{(n^2 + n + n^2\kappa^2)^2 + (1 + n)^2 + 2n^2\kappa^2}{((1 + n)^2 + n^2\kappa^2)^2},$$

or towards about 0.6 for carbon particles. Fig. 5 shows the changes in the proportion of diffracted or scattered light for carbon particles of various sizes.

Angular Distribution of the Deflected Light

The amount of light that is deflected by a spherical obstacle depends on the angle between the direction considered and the direction of the incident wave. The variation of the intensity with the angle merits examination on account of its close relation to the size of the particle.

When a spherical particle is placed in the path of a plane unpolarized wave of strong monochromatic light, the intensity of the scattered light observed in a direction that forms the arbitrary angle γ with the incident beam sent along the horizontal or z-axis is obtained by the simple addition of the two polarized components $I_{|}$ and $I_{||}$. The intensity $I_{|}$ is the intensity of the light whose electrical vibration is perpendicular to the plane containing the line of vision and the incident ray, and $I_{||}$ is the intensity of the light whose electric vector oscillates in the plane determined by the line of vision and the incident ray. When the distance r separating observer and particle is a large multiple of a, the general formulae for the intensity $I_{|}$ and $I_{||}$ are

$$I_{|} = \frac{1}{\rho^2}\left|\sum_1^\infty \left(\frac{a_\nu}{\nu(\nu + 1)}\Pi_\nu + \frac{p_\nu}{\nu(\nu + 1)}(v\Pi_\nu - (1 - v^2)\Pi'_\nu)\right)\right|^2$$

$$I_{||} = \frac{1}{\rho^2}\sum_1^\infty \left(\frac{a_\nu}{\nu(\nu + 1)}(v\Pi_\nu - (1 - v^2)\Pi'_\nu) + \frac{p_\nu}{\nu(\nu + 1)}\Pi_\nu\right)\Bigg|^2,$$

where

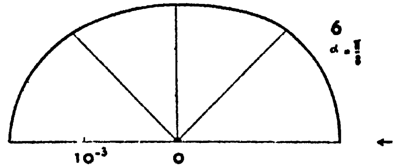
$$v = \cos\gamma$$

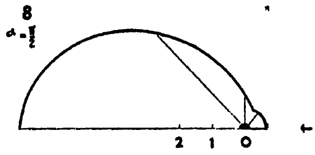
$$\rho = \frac{2\pi r}{\lambda} m_0$$

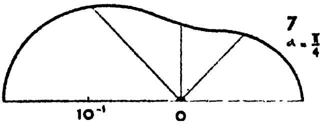
$$\Pi_\nu = \frac{1}{2^\nu}\sum_0^{\frac{\nu+1}{2}-1} (-1)^s \frac{(2\nu - 2s)!\, v^{\nu-2s-1}}{(\nu - s)!\, s!(\nu - 2s - 1)!}$$

When the upper limit of $s = (\nu + 1)/2$ is half an integer, this particular value must not be considered in evaluating Π_ν.

The sums $(I_{\text{I}} + I_{\text{II}})$ to be expected at a given large distance from carbon particles of different diameters have been calculated, and are represented in Figs. 6 to 9 along the directions for which they are valid; the small spheres are assumed to be of such size that when illuminated with light of a constant wave-length the ratio $2a/\lambda$ is a multiple of $\frac{1}{8}$. Grains for which $2a/\lambda$ is less than $\frac{1}{8}$ are seen to diffuse light uniformly in all directions. For ratios from $\frac{1}{4}$ upwards, light is deflected only slightly from the direction of the incoming ray. For $2a/\lambda = \frac{1}{2}$, for instance, by far the larger part of the light coming from the particle is confined to the space within the angles 120° and 240°. With still larger spheres (Fig. 9) only a narrow main beam, accompanied by a few unimportant side lobes, remains and very little light is visible at right angles to the direction of the incoming wave.







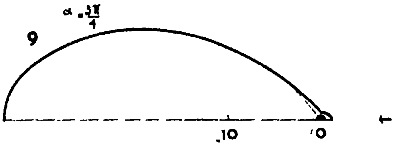


FIG. 6. *Distribution of scattered light of a given wave-length around a spherical carbon particle for which* $2a/\lambda = \frac{1}{8}$. *The light is coming from the right.*

FIG. 7. *Distribution of scattered light around a spherical carbon particle for which* $2a/\lambda = \frac{1}{4}$.

FIG. 8. *Distribution of scattered light around a spherical carbon particle for which* $2a/\lambda = \frac{1}{2}$.

FIG. 9. *Distribution of scattered light around a spherical carbon particle for which* $2a/\lambda = \frac{3}{4}$. *Scale units are 10,000 times as large as those used for* $2a/\lambda = \frac{1}{8}$ *and 100 times as large as those used for* $2a/\lambda = \frac{1}{4}$.

As regards the intensity of the radiation at a given distance, only a small amount of light is diffused by particles having a diameter less than one-eighth of the wave-length of the incident light. For $2a/\lambda = \frac{1}{8}$, the light contributed by 10,000 particles is required to equal the intensity obtained in any direction from a sphere for which $2a/\lambda = \frac{3}{4}$. According to the formula valid for the smallest particles,

$$\frac{\lambda^2}{16\pi^2 r^2}\,|a_1|^2$$

in any direction. When the volume $V = 4\pi a^3/3$ is introduced, this expression can be written

$$\frac{9V^2}{4r^2\lambda^4}\,\frac{|a_1|^2}{\alpha^6} = \frac{9V^2}{r^2\lambda^4}\,\frac{(n - in\kappa)^2 - 1}{(n - in\kappa)^2 + 2}$$

whereas $I_{\parallel}$ is negligible. That is to say, the intensity of the scattered light in any direction at a distance r from a carbon sphere for which $2a/\lambda$ is less than about $\frac{1}{10}$ is proportional to the sixth power of the radius a and inversely proportional to the fourth power of the wave-length. A steep increase in the intensity of scattered light occurs therefore with increase in diameter. But for larger and larger obstacles, the outgoing light becomes concentrated along the direction of the incoming ray; the intensity of this light varies more nearly as the volume or mass of the particle of carbon, or even less steeply. When, for instance, the intensities obtained behind a spherical obstacle for which $2a/\lambda = 0.5$ are multiplied by $3\frac{3}{8}$ (the ratio between the volumes or masses of spheres for which $2a/\lambda = 0.5$, in one case, and $2a/\lambda = 0.75$ in the other), the results obtained exceed the values given by the larger particles, or are at least of the same order of magnitude (Figs. 8 and 9).

Polarization of Scattered Light

In the light deflected and scattered by the particle along a given horizontal direction, the intensity furnished by the vibration that occurs parallel to the vertical or x-axis is no longer equal to the intensity of the vibration in the horizontal plane. There is therefore in the scattered light an excess $I_{|} - I_{\parallel}$ or a fraction $(I_{|} - I_{\parallel})/(I_{|} + I_{\parallel})$ of polarized light. The vibrations are parallel to the vertical axis when the fraction is positive, and parallel to the plane passing through the incident ray and the direction of vision when it is negative. The fraction varies with the angle γ and the size of the particles. For light scattered by molecules, the radiation emitted in a direction that forms 90° with the incoming ray is completely polarized, the electrical vibrations occurring in the direction that is normal to the plane passing through the incoming and the outgoing rays. The same result is obtained with small spherical carbon particles, as long as the ratio $2a/\lambda$ is less than about $\frac{1}{4}$. When this fraction exceeds $\frac{1}{4}$, the polarization is never quite complete whatever the direction of vision, but the percentage of polarized light attains a maximum for a certain angle or for several angles. For $2a/\lambda = \frac{1}{2}$, the maximum is equal to about $\frac{3}{8}$ near 90°; for $2a/\lambda = \frac{3}{4}$ there occurs almost complete polarization for an angle of 60°, where however the intensity of scattered light is very weak; for directions between 80° and 110° the electrical vibrations in the very faint scattered radiation are parallel to the plane containing the incoming ray and the direction of vision. At 120° the extent of polarization passes through a second peak of about 50%. This variation is a useful indication of the size of the particles.

Practical Applications

The light transmitted or scattered by a single grain of carbon is too weak to be studied; but if a small cloud of particles of similar sizes is contained within a small space, the angles between the incoming and outgoing rays remain virtually unchanged for a distant observer, whatever the particle chosen, and the formulae remain valid for the total radiation received from the accumulation of N particles.

The most straightforward application of the theory consists of the calculation of the optical properties that a known number of carbon particles of diameter $2a$ suspended in unit volume of air would possess either in white or in monochromatic light.

In practice the reverse problem may also occur; when absorption and scattering per unit volume have been determined experimentally, the concentration of the particles and their size, if approximately uniform, have to be found. If it is possible to measure the relative amount of scattered light at a few angles and for one state of polarization, and if the intensities obtained are plotted as a function of the angles, a comparison of the curve with the theoretical curves for different values of $2a/\lambda$ (Figs. 6 to 9, for instance) suggests an approximate value for the diameter of the particle. A uniform distribution of the diffused light is proof of a diameter less than about $\lambda/10$; absence or weakness of scattered light along directions that form acute angles with the direction of the incident wave points to the presence of coarse carbon sphericles for which $2a/\lambda$ is greater than $\frac{1}{2}$.

As soon as the size is known, the coefficient of absorption can be computed for one particle in unit volume, and the number of particles N can be deduced from the measured absorption per unit volume of suspension. The result arrived at for the concentration of the spheres can be verified by measuring the actual intensity of the diffused light, expressed as a fraction of the incident light, along at least one direction of observation, and by comparing it with the calculated intensity for N grains of carbon.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. APRIL, 1942 NUMBER 4

OPERATIONAL METHODS OF DEALING WITH CIRCUITS EXCITED BY SINUSOIDAL IMPULSES[1]

BY W. B. COULTHARD[2]

Abstract

A method is developed of deducing operational expressions for complex wave forms such as repeated sinusoidal impulses. By the use of the Heaviside expansion theorem, formulae are obtained for the current flowing in a circuit consisting of a condenser and a loading resistance when fed from a straight line rectifier.

Nowadays, especially in the field of communication engineering, e.m.f's having wave shapes much different from sinusoidal shape are used. This paper shows that it is possible to determine the effects of such e.m.f's in a circuit by operational methods without resort to Fourier's analysis. Here the output of a rectifier circuit will be considered: of course, the method is applicable equally to waves of any shape. The solution of the differential equations is obtained by means of the Heaviside expansion theorem as being more familiar to engineers, though mathematicians prefer to proceed by using the Bromwich contour integral. In Section (i), methods of obtaining the operational expressions for the impulse and for repeated impulses are developed. This method is based on work by Jeffreys (3). In Sections (ii) and (iii) the result is applied to the output of a rectifier circuit.

(i) Operational Expression for an Impulse and for a Train of Repeated Impulses

From a consideration of Taylor's theorem it can be shown that $\epsilon^{-\alpha p}f(t) = f(t - \alpha)$. In circuit theory this means that the switch closure is delayed until a time $t = \alpha$ after the start of count of time, so the function $f(t - \alpha)$ can be written as $\epsilon^{-\alpha p}f(t)$. Replacing $f(t)$ by E, we have next an expression as $[\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p}]E$. This means that a positive voltage E is applied to the circuit at a time $t = \alpha_1$; at some time later ($t = \alpha_2$) an equal but negative voltage is applied. The resultant voltage impulse is therefore a "square" wave of amplitude E of duration $(\alpha_2 - \alpha_1)$ seconds.

---

[1] *Manuscript received in original form December 24, 1941, and as revised, February 18, 1942.*
Contribution from the Department of Mechanical and Electrical Engineering, The University of British Columbia, Vancouver, B.C.

[2] *Assistant Professor of Electrical Engineering.*

When the impulse deviates from a constant amplitude the wave form may be regarded as a series of vertical strips. Then

$$(\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p})f(\alpha_1) + (\epsilon^{-\alpha_2 p} - \epsilon^{-\alpha_3 p})f(\alpha_2) + \cdots\cdots = E(t),$$

or

$$E(t) = \sum_{r=1}^{\infty} f(\alpha_r)[\epsilon^{-\alpha_r p} - \epsilon^{-\alpha_{r+1} p}].$$

On making the intervals $[\alpha_1\alpha_2]$, $[\alpha_2\alpha_3]$, - - - exceedingly small, in the limit we obtain

$$E(t) = -\int_{-\infty}^{\infty} f(\alpha)d[\epsilon^{-\alpha p}].$$

On treating p as a parameter, as in Carson's work, we get on letting

$$E(t) \doteqdot g(p) \cdot 1$$

that

$$g(p) = \int_{-\infty}^{\infty} pf(\alpha)\epsilon^{-\alpha p}d\alpha.$$

For practical work $f(\alpha)$ vanishes when α is negative so that only the range of α from 0 to $+\infty$ need be considered. We get the Carson integral equation

$$g(p) = \int_{0}^{\infty} pf(\alpha)\epsilon^{-\alpha p}d\alpha.$$

Likewise for an impulse of limited duration T say, $f(\alpha)$ vanishes when α is greater than T, so follows

$$g(p) = \int_{0}^{T} pf(\alpha)\epsilon^{-\alpha p}d\alpha.$$

When the impulse is repeated in the same sense every T seconds, the wave train may be formulated by

$$[1 + \epsilon^{-pT} + \epsilon^{-2pT} + \cdots][\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p}]E = E(t).$$

By summation

$$E(t) = \frac{\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p}}{1 - \epsilon^{-pT}} \cdot E,$$

i.e., the operational expression for a repeated unidirectional impulse is obtained by multiplying the operational expression of the impulse by the inverse of $[1 - \epsilon^{-pT}]$. It is readily shown for the case where the impulse is positive and negative alternately that the train is obtained by multiplying by the inverse of $[1 + \epsilon^{-pT}]$.

(ii) Operational Expression for Rectified Sine Waves

We now apply the foregoing theory to the case of rectified sine waves. Consider first the impulse; this is formulated by $E \sin \omega t$ in the interval $[0,\pi]$, so

$$g(p) = p\int_{t=0}^{\pi/\omega} \epsilon^{-pt} \sin \omega t \, dt.$$

On integration this yields $g(p)=\frac{\omega p}{p^2+\omega^2}\left(1+\epsilon^{-\pi p/\omega}\right)$.

When this impulse is repeated in the same sense as in a full wave rectifier,

$$g(p) = \frac{\omega p}{p^2+\omega^2}\cdot\frac{1+\epsilon^{-\pi p/\omega}}{1-\epsilon^{-\pi p/\omega}}.$$

In the case of the single phase rectifier the wave is repeated at intervals of 2π and we get eventually that,

$$g(p) = \frac{\omega p}{p^2+\omega^2}\cdot\frac{1+\epsilon^{-\pi p/\omega}}{1-\epsilon^{-2\pi p/\omega}}.$$

As a final example in this section we consider the case of the chopped wave. Let the wave occur only in the interval $[\delta, \pi-\delta]$. So

$$g(p) = p\int_{\delta/\omega}^{\overline{\pi-\delta}/\omega}\epsilon^{-pt}\sin\omega t\,dt.$$

Evaluation of the integral gives, after some work,

$$g(p) = \frac{p^2}{p^2+\omega^2}\left[\epsilon^{-\delta p/\omega}(\sin\delta+\omega/p\cos\delta) - \epsilon^{-\overline{\pi-\delta}p/\omega}(\sin\delta-\omega/p\cos\delta)\right].$$

This expression is general. On substituting $\delta = \pi/3$ the operational expression for a wave in the interval $[\pi/3, 2\pi/3]$ is obtained as,

$$g(p) = \frac{p^2}{p^2+\omega^2}\left[\epsilon^{-\pi p/3\omega}\left(\frac{\sqrt{3}}{2}+\omega/2p\right) - \epsilon^{-2\pi p/3\omega}\left(\frac{\sqrt{3}}{2}-\omega/2p\right)\right].$$

This is the operational expression for the "ideal" voltage wave of a three phase rectifier.

(iii) Current Response in a Simple Circuit

From standard theory the operational impedance may be written in the form $Z(p)$ when all the circuit parameters are invariable. The current due to a voltage $E.g(p)$ will be given by the equivalency $i(t) \doteqdot Eg(p)/Z(p)$. Using the arguments developed by Dalzell (2) we have, if

$$g(p) = p\int_0^\infty \epsilon^{-pt}f(t)dt,$$

then by inversion the value of

$$f(t) = \frac{1}{2\pi i}\int_L \frac{g(z)}{z}\epsilon^{zt}dz.$$

So we have here that

$$i(t) = \frac{1}{2\pi i}\int_L E\frac{g(z)}{z}\frac{\epsilon^{zt}}{Z(z)}dz.$$

This contour integral is readily solved in many cases by the Heaviside expansion theorem: in others it is necessary to revert to the original expression for a solution.

To illustrate the procedure we consider some features of a rectifier circuit with a leaky smoothing condenser, whose operational impedance is given by $[R + 1/Cp]$.

(*a*) For a wave $E \sin \omega t$ in the interval $[0,\pi]$, and zero thereafter acting on the condenser there are the following operational equivalencies for the current:—

In the period $0 < t < \pi/\omega$.

$$i(t) \doteqdot E \frac{\omega p}{p^2 + \omega^2} \cdot \frac{Cp}{1 + RCp}, \qquad (1)$$

where R is the leakage resistance of the condenser and C its capacity. This gives the well known result (1) for the charging current,

$$i(t) = \frac{\omega EC}{\sqrt{1 + \omega^2R^2C^2}} \left[\sin \overline{\omega t + \phi} - \frac{\epsilon^{-\alpha t}}{\sqrt{1 + \omega^2R^2C^2}} \right],$$

with $\tan \phi = 1/\omega RC$ and $\alpha = 1/CR$.

For the period $t > \pi/\omega$,

$$i(t) \doteqdot \frac{E}{R} \frac{\omega p}{p^2 + \omega^2} \cdot \frac{p}{p + \alpha} (1 + \epsilon^{-\pi p/\omega}). \qquad (2)$$

Here the effective root is $p = -\alpha$, since the roots $p = \pm j\omega$ have no residue due to the term $(1 + \epsilon^{-\pi p/\omega})$. We have

$$i(t) = -\frac{\omega CE\, \epsilon^{-\alpha t}}{1 + \omega^2R^2C^2} (1 + \epsilon^{\pi \alpha/\omega})$$

as the discharge current.

The exact point of change-over from Condition (1) to Condition (2) requires further investigation, but will not be considered for this particular case.

(*b*) When the wave $E \sin \omega t$ is repeated in the same sense and is applied to a loading resistance in parallel with a smoothing condenser, we have with I_1 as the current through the condenser, I_2 that through the resistance, and I the total current, on assuming a loss free condenser, that

$$\frac{I_1}{pC} = I_2R.$$

$$I_1 + I_2 = I.$$

Also

$$I = \frac{E}{R} \cdot \frac{p\omega}{p^2 + \omega^2} \frac{1 + \epsilon^{-\pi p/\omega}}{1 - \epsilon^{-\pi p/\omega}} (1 + RCp).$$

$\therefore$

$$I_1 = EC \frac{p^2\omega}{p^2 + \omega^2} f(\pi p/\omega)$$

and

$$I_2 = \frac{E}{R} \cdot \frac{p\omega}{p^2 + \omega^2} f(\pi p/\omega).$$

These operational expressions show that I_2 is in phase with the voltage whilst I_1 is out of phase by $\pi/2$. Dealing with the case of $t > \pi/\omega$ the load current is obtained, with roots $p = \pm j2n\omega$, as

$$\frac{E}{R} \cdot \frac{2\omega^2}{\omega^2(1 - 4n^2)} \frac{\epsilon^{j2n\omega t}}{\pi} + \frac{2}{\pi} \frac{E}{R} \cdot \frac{\epsilon^{-j2n\omega t}}{1 - 4n^2}$$

The total contribution is

$$\frac{4}{\pi}\,\frac{E}{R}\,\frac{\cos 2n\omega t}{1 - 4n^2},$$

where n has values 1 to infinity.

At $p = 0$ the residue is $\frac{2}{\pi}\,\frac{E}{R}$, and so the total current through the resistance is

$$I_2 \quad \frac{2}{\pi}\,\frac{E}{R}\left[1 - 2\sum_1^\infty \frac{\cos 2n\omega t}{4n^2 - 1}\right].$$

In similar manner the current through the condenser is

$$I_1 = \frac{8}{\pi}\,E\omega C \sum_1^\infty \frac{n \sin 2n\omega t}{1 - 4n^2}.$$

From the characteristics of the circuit, certain features, such as the "cut off" and "striking" potentials, can be derived. At some value of ωt the current $I = 0$, i.e., $I_1 = -I_2$. The condenser discharges through the resistance. Let this value of ωt be ψ_2, defined by:—

$$4\omega CR \sum_1^\infty \frac{n \sin 2n\psi_2}{4n^2 - 1} - 1 + 2\sum_1^\infty \frac{\cos 2n\psi_2}{4n^2 - 1} = 0.$$

For values of $\omega t > \psi_2$ the condenser continues to discharge until the applied voltage of the following half wave is equal to that across the condenser. For the condenser discharge,

$$Rpq + q/C = 0,$$

with the boundary condition at $t = 0$, $q = Q_0$. It has been shown (1) under this condition that

$$q \doteqdot Q_0 \frac{p}{p + 1/CR} = Q_0 \epsilon^{-t/CR}.$$

The voltage across the condenser is given by

$$v(t) = \frac{Q_0}{C}\,\epsilon^{-t/CR}.$$

As Q_0/C must be equal to the voltage at cut off we may write

$$v(t) = E \sin \psi_2\, \epsilon^{-t/CR},$$

with t measured from the instant $\omega t_0 = \psi_2$. When $v(t)$ is equal to the rising voltage of the next half wave of the rectifier, the striking voltage (ψ_1) is defined by

$$E \sin \psi_1 = E \sin \psi_2 \epsilon^{-(\pi - \psi_2 + \psi_1)/\omega CR}.$$

(c) We now consider the effects of these discontinuities on rectifier operation. We assume an ideal rectifier, i.e., one having zero forward resistance and an infinite value of the inverse resistance. For the two zones of voltage,

$$g(p) \doteqdot E\left[p\int_{\psi_1/\omega}^{\psi_2/\omega} \epsilon^{-pt} \sin \omega t\, dt + p\int_{\psi_2/\omega}^{\overline{\pi+\psi_1}/\omega} \epsilon^{-pt} \sin \psi_2 \cdot \epsilon^{-t/CR} dt\right]$$

We now shift the time axis with ψ_1/ω as zero, then ψ_2 becomes $\psi_2 - \psi_1 = \theta$. On integration

$$g(p) = E\left[\frac{p^2}{p^2+\omega^2}\left\{\frac{\omega}{p} - \epsilon^{-\theta p/\omega}\left(\sin\theta + \frac{\omega}{p}\cos\theta\right)\right\}\right.$$
$$\left. + \sin\theta\,\frac{p}{p+\alpha}\left\{\epsilon^{-\overline{p+\alpha}\theta/\omega} - \epsilon^{-\overline{p+\alpha}\pi/\omega}\right\}\right].$$

where $\alpha = 1/CR$.

The term within the first bracket gives the operational expression for the voltage in the interval $[0,\theta]$, while the second term gives that for the interval $[\theta,\pi]$. The load current is now given by

$$i_2 \doteq \frac{E}{R}\,\frac{g(p)}{1-\epsilon^{-\pi p/\omega}}\,.$$

Inspection shows residues at $\pm j\omega$, $\pm j2n\omega$, $-\alpha$ and zero. Evaluation gives after some simplification that

$$i_2 = \frac{E}{\pi R}\left\{1 - \cos\theta + \overline{\pi - \theta}\sin\theta + \sum_1^\infty \frac{4n}{1-4n^2}\left[\frac{\cos 2n\omega t}{2n} - \right.\right.$$
$$\left.\frac{\cos\theta\cos 2n(\omega t - \theta)}{2n} + \sin\theta\sin 2n(\omega t - \theta)\right] +$$
$$\left.2\omega\sin\theta\sum_1^\infty\left[\frac{\epsilon^{-\alpha\theta/\omega}\cos\overline{2n(\omega t - \theta) - \phi_n} - \epsilon^{-\alpha\pi/\omega}\cos\overline{2n\omega t - \phi_n}}{\sqrt{\alpha^2 + 4n^2\omega^2}}\right]\right\}$$

The second summation term gives the current during the discharge period $[\theta,\pi]$. It will be noted that the current depends *inter alia* on the capacity of the condenser and on the resistance of the load. When the time constant of the circuit is small, the discharge of the condenser is rapid and the voltage thereon may be reduced to zero before the applied voltage reaches zero.

Conclusion

The application of standard operational methods to circuits excited by complex wave forms has been discussed. The solutions are deduced readily even though the mathematics are cumbersome. The solutions are obtained in the form of a series and for calculation purposes the first few terms are sufficient in the majority of cases.

References

1. Coulthard, W. B. Transients in electric circuits. Pitman. 1941.
2. Dalzell, D. P. Proc. Phys. Soc. London, 42 : 75-81. 1930.
3. Jeffreys, H. Operational methods in mathematical physics. 2nd ed. Cambridge University Press. 1931.
4. McLachlan, N. W. Phil. Mag. 24 : 1055-1058. 1937.

THE INFLUENCE OF SAMPLE COMPOSITION ON MAGNESIUM, CADMIUM, AND LEAD INTENSITY RATIOS AS RADIATED FROM A SPARK SOURCE[1]

BY G. O. LANGSTROTH[2] AND K. B. NEWBOUND[3]

Abstract

Marked variations have been observed in the relative intensities of magnesium, cadmium, and lead lines on the addition of various amounts of foreign substances to standard samples and excitation in a condensed spark source. The changes in the interspectra intensity ratios depended on the nature and amount of the added substances, as well as on the elements under consideration. In many instances buffering of the samples with sodium potassium tartrate or potassium nitrate did not reduce the variations. The behaviour cannot be explained solely on the basis of changes in an "effective" discharge temperature. The data permit no obvious generalization that might be helpful as a criterion for the choice of internal standard elements and buffer substances.

Introduction

The accuracy of spectrographic analyses is largely determined by the constancy of the relation between the relative intensities of spectral lines radiated by the source and the amounts of the corresponding elements present in the samples. Spectrographic methods are being applied successfully in the analysis of samples that do not vary markedly in general composition (e.g., alloys). Application in the analysis of samples that do so vary, however, is more difficult if results of high accuracy are desired. This circumstance arises from the fact that the intensity ratio of chosen lines of two elements may depend to some extent on the extraneous composition of the samples. Numerous examples of such a dependence have been noted (1, 2, 5, 9, 10), and special techniques have been developed to deal with it under specific conditions. The general problem however has received little attention, and the factors that must be carefully controlled if such effects are to be minimized remain unknown.

This article describes a preliminary study of the changes that occur in the relative intensities of certain spectral lines when various amounts of foreign substances are added to "standard" samples. The results, over the limited range of these experiments, indicate that the intensity ratio variations depend both on the nature and the amount of the added substance, and are commonly different for different line pairs. In some instances certain ratios tended toward "saturation" values at the greatest additions, but this behaviour was not general. The presence of a buffer did not always improve the constancy of the ratios; it did improve the reproducibility under any particular set of

---

[1] *Manuscript received in original form January 26, 1942, and as revised, February 23, 1942. Contribution from the Physics Department, University of Manitoba, Winnipeg, Man.*

[2] *Associate Professor of Physics.*

[3] *Holder of a Bursary under the National Research Council of Canada.*

conditions. Its efficiency apparently depended on the elements under consideration and on the nature of the change in extraneous composition, as well as on the nature of the buffer itself and the amount used. It has not been possible to generalize the results, and no correlation is apparent between the extent of the intensity changes and the characteristics of the added substances (e.g., ionization potentials of constituents ,vapour pressure, stability, etc.). The results cannot be interpreted solely on the basis of changes in an "effective" discharge temperature on the addition of foreign substances (cf. 4). The explanation is probably complex, and must await the compilation of additional data.

Experimental

The sparking circuit proper consisted of a 0.03 microfarad condenser, a 120 microhenry inductance, and a spark gap connected in series. The condenser was connected directly across the secondary of a transformer whose primary voltage was controlled by an auto-transformer. In operation the primary voltage was adjusted to the minimum value consistent with the occurrence of a single spark on every half cycle of the line voltage. The electrodes were of the point-movable-plane type (3); both were copper. The area of the plane electrode was 1.2×1.0 cm.^{2}. An electrode separation of 3.1 mm. was used throughout the work.

Spectra were photographed with a medium quartz spectrograph constructed at the University. For the major part of the work no condensing lens was used. In order to investigate line intensities emitted from different parts of the discharge an image of the source was focused on the spectrograph slit with the aid of a quartz-fluorite lens.

The standard sample contained 0.125, 1.00, and 1.00 mg. per cc. of magnesium, cadmium, and lead respectively (as chlorides). The intensity ratios of chosen lines of these elements were measured with and without the addition of various amounts of extraneous substances. The extraneous substances were the chlorides of potassium, lithium, and calcium, boric acid, and ammonium chloride. These substances were used in amounts that involved comparable numbers of molecules. Similar experiments were carried out with the samples buffered with sodium potassium tartrate, and with potassium nitrate in three different concentrations.

The prepared solution (0.050 cc.) was deposited on the plane electrode and evaporated to dryness under reduced pressure. Deposits that showed appreciable non-uniformity were discarded. The electrode was sparked for 15 sec., during which the spark passed over the entire surface of the plane electrode, tracing out a multiple W pattern and continually striking a fresh surface of the deposit. Some reproducibility was sacrificed in the adoption of this short exposure time, but it was desired that the spark should not strike to some part of the surface whose conditions had been changed by a preceding spark. In some instances sparking periods of 20 and of 25 sec. were used.

A complete series of spectra were photographed on each plate along with plate calibration spectra produced by a step-sector and brass arc. Intensity measurements were made by the usual microphotometric method (7). Since the intensity ratio of two lines differing considerably in wave-length was given in terms of the relative intensities of two lines of the brass arc, comparison of the ratio as given by two plates was permitted only through measurements on spectra common to both. The spectral lines investigated are given in Table I.

TABLE I

SPECTRAL LINES INVESTIGATED*

Emitter	Ground state, cm.$^{-1}$	Wave-length, Å	Classification	Initial level, cm.$^{-1}$	Final level, cm.$^{-1}$
Mg (atom)	61672	2852.1	$3s^2\,{}^1S_0 - 3s3p\,{}^1P^0_1$	26621	61672
		2779.8	$3s3p\,{}^3P^0_{2,1} - 3p^2\,{}^3P_{2,1}$	3799 3840	39761 39801
Mg (ion)	121267	2936.5	$3p\,{}^2P^0_{3/2} - 4s\,{}^2S_{1/2}$	51462	85506
Cd (atom)	72539	3261.1	$5s^2\,{}^1S_0 - 5s5p\,{}^3P^0_1$	41883	72539
		3403.7	$5s5p\,{}^3P^0_0 - 5s5d\,{}^3D_1$	13052	42425
Pb (atom)	59821	2833.1	$6p^2\,{}^3P_0 - 6p({}^2P_{1/2})7s\,2^0_1$	24536	59821
		2614.2	$6p^2\,{}^3P_1 - 6p({}^2P_{1/2})6d\,3^0_1$	13754	52004
		3639.6	$6p^2\,{}^3P_1 - 6p({}^2P_{1/2})7s\,2^0_1$	24536	52004

* *The lines in this table are limited to those for which data are presented in the article.*

Results

Typical results are presented in Table II for Mg 2852 Å, Cd 3261 Å, and Pb 2833 Å. The data refer to radiation from the entire discharge, i.e., no condensing lens was used. The symbols *A*, *B*, *C*, *D*, and *E* refer to different buffering conditions, as follows:

A: no buffer was used
B: sodium potassium tartrate buffer (384×10^{-7} gm. per mm.^{2})
C: potassium nitrate buffer (69×10^{-7} gm. per mm.^{2})
D: potassium nitrate buffer (138×10^{-7} gm. per mm.^{2})
E: potassium nitrate buffer (277×10^{-7} gm. per mm.^{2})

The amount of buffer is given in mass of salt per square millimetre of electrode. The ratios for the unbuffered sample with no extraneous addition have been set equal to unity, and all other ratios are given in these terms. In each instance the amounts of magnesium chloride, cadmium chloride, and lead chloride per square millimetre of electrode were respectively, 2.0×10^{-7}, 6.8×10^{-7}, and 5.6×10^{-7} gm.—a total salt load of 14.4×10^{-7} gm. per mm.^{2}.

TABLE II

EFFECT OF ADDITIONS OF EXTRANEOUS SALTS ON INTENSITY RATIOS

Additions, mg./mm.^{2} × 10^7		A No buffer			B Sodium potassium tartrate buffer, 384 × 10^{-7} gm./mm.^{2}			C Potassium nitrate buffer, 69 × 10^{-7} gm./mm.^{2}			D Potassium nitrate buffer, 138 × 10^{-7} gm./mm.^{2}			E Potassium nitrate buffer, 277 × 10^{-7} gm./mm.^{2}		
		Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Cd/Mg	Pb/Cd
None		1.00	1.00	1.00	0.97	0.82	1.18	1.14	0.70	1.63	1.09	0.59	1.85	1.14	0.52	2.19
LiCl	1.0	0.92	1.00	0.92	—	—	—	1.18	0.76	1.53	1.05	0.50	2.07	1.08	0.45	2.39
	2.0	0.79	0.95	0.83	—	—	—	1.24	0.72	1.72	1.22	0.59	2.07	1.03	0.45	2.25
	4.0	0.85	0.95	0.89	0.97	0.76	1.26	1.20	0.72	1.69	1.18	0.60	1.96	1.03	0.45	2.27
	8.1	1.02	0.96	1.06	0.98	0.79	1.24	1.18	0.67	1.74	1.18	0.49	2.40	1.16	0.46	2.54
	16.3	1.07	0.93	1.15	0.89	0.72	1.23	1.20	0.70	1.72	1.20	0.47	2.54	1.19	0.41	2.93
	32.6	1.08	0.80	1.35	0.89	0.79	1.13	1.12	0.61	1.82	1.23	0.47	2.60	1.03	0.34	3.02
$CaCl_2 . 6H_2O$	4.5	0.94	1.05	0.90	—	—	—	1.33	0.78	1.69	1.05	0.59	1.78	1.17	0.55	2.25
	9.1	0.95	—	—	—	—	—	1.30	0.72	1.79	—	0.54	—	1.15	0.54	2.12
	18.4	0.87	1.10	0.79	0.82	0.83	0.99	1.12	0.73	1.55	1.12	0.59	1.90	1.22	0.55	2.20
	36.7	0.78	0.75	1.04	0.83	0.80	1.04	1.05	0.70	1.65	1.03	0.55	1.84	1.09	0.51	2.15
	73.0	0.78	0.80	0.97	0.84	0.70	1.20	0.97	0.70	1.40	0.80	0.49	1.63	0.63	0.46	1.36
	146.	0.83	0.65	1.28	1.08	0.48	2.25	0.94	0.58	1.60	0.72	0.49	1.46	0.75	0.41	1.82
NH_4Cl	1.1	0.98	1.15	0.85	—	—	—	1.15	—	—	1.09	—	—	1.04	0.52	2.01
	2.3	0.99	1.08	0.92	—	—	—	1.08	0.71	1.50	1.10	0.55	2.00	1.14	0.51	2.23
	4.6	0.97	1.00	0.97	—	—	—	1.08	0.75	1.45	1.14	0.67	1.68	1.17	0.51	2.10
	9.2	1.03	1.20	0.86	0.85	0.73	1.17	1.23	0.68	1.80	1.16	0.62	1.87	1.23	0.52	2.38
	18.4	1.05	1.00	1.05	0.81	0.81	0.99	1.34	0.71	1.89	1.17	0.64	1.84	1.30	0.86	1.51
	36.7	0.87	0.72	1.20	0.77	0.75	1.03	1.32	0.63	2.10	1.29	0.82	1.58	1.41	0.96	1.46

An analysis of the percentage variations of the ratios given in Table II is presented in Fig. 1. Figs. 2 and 3 present typical data concerning the values of the intensity ratios in light coming from different parts of the discharge for samples of different extraneous composition. Typical data on the behaviour of the intensity ratio of an ionized to a neutral atom spectrum line on addition of extraneous material are given in Fig. 4.

Discussion

Owing to the requirement for a short sparking period in these experiments high reproducibility of results was not attained. The error in the ratios is probably less than 10%, as indicated by repeated measurements on identical samples, but in rare instances it may slightly exceed this value. A plot of the deviations of intensity ratios from the mean for a group of samples differing

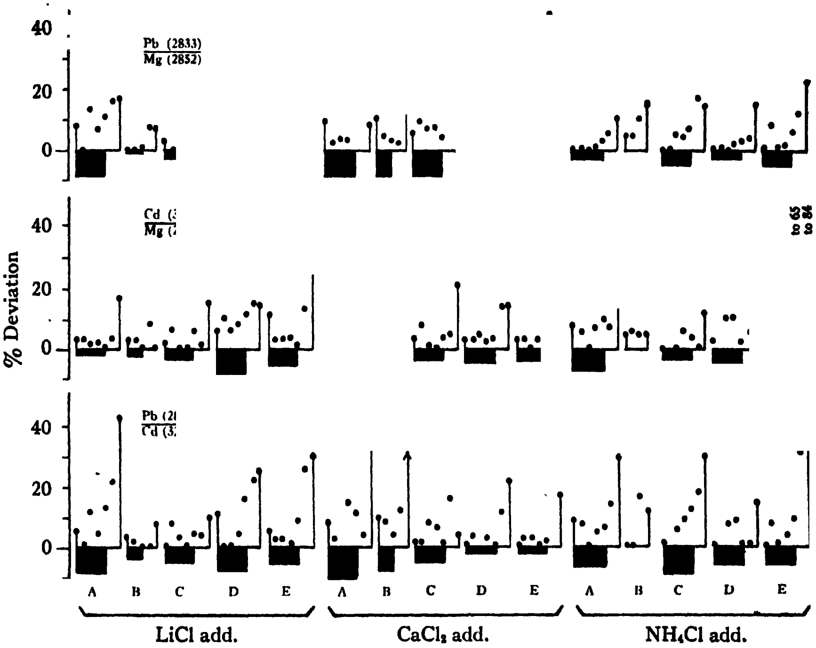


FIG. 1. *Percentage variations of intensity ratios from the mean for 'small' additions. The samples are considered in groups, each group consisting of samples buffered in the same way and with the same kind of extraneous material added. The mean value of the intensity ratios for each line pair in each group has been taken as that for 'small' additions (i.e., not greater than 8.1×10^{-7}, 36.7×10^{-7}, and 9.2×10^{-7} gm. per mm.^{2} of lithium chloride, calcium chloride, and ammonium chloride respectively), since in general the larger additions resulted in marked changes in the ratios. The percentage deviation of each ratio in the group from this mean is denoted by a dot above the zero line. The deviations within a group are plotted with additions of extraneous material increasing toward the right; the left-hand dot in each group represents the deviation for the sample with no addition. The depths of the blocks below the zero line represent the average deviation of the ratios for samples with small additions, and their lateral extent indicates the samples included in the mean. The symbols A, B, C, D, and E denote the buffering conditions and have the same significance as in Table II.*

only in extraneous composition shows many instances in which the variations in the ratios cannot be attributed to experimental error (Fig. 1). In general, large variations in composition resulted in marked changes in the ratios (Fig. 1 and Table II). Under actual conditions of analysis smaller variations are, perhaps, to be expected, since conditions assumed to give the maximum effect were chosen for these experiments, i.e., the spark continually advanced to a fresh deposit of material. This choice of conditions was made in the hope of ascertaining some of the factors more closely related to the intensity variations.

(a) Results for Unbuffered Solutions

While some of the variations given in Table II, Condition *A*, are not large, the data show definite trends that are believed to be significant. It has been noted by some workers (2) that certain intensity ratios tend toward "saturation" values as the concentration of a particular substance in the sample is increased. This observation does not appear to hold generally over the range of the present investigation. It does hold in several instances, e.g., with the addition of increasing amounts of potassium nitrate (as a buffer) the Cd/Mg ratio decreased from 1.00 to 0.70 to 0.59 to 0.52 (Table II).

The substances used as additions in these experiments were chosen mainly with respect to the ionization potential of the most easily ionized constituent; they represent a series containing atoms of 4.3, 5.4, 6.1, 8.4, and 13.0 volts ionization potential. The results for the first and fourth of these are not included in the article. The data show no obvious relation between this characteristic and the effect of the addition on the ratios, nor do they suggest any clear cut dependence on other physical characteristics (e.g., vapour pressure, stability, etc.). Furthermore, the effect of an addition depends on the particular line pair under consideration, e.g., addition of the largest amount of lithium chloride used increased the Pb/Cd ratio by 35% but decreased the Cd/Mg ratio by 20%.

(b) Results for Buffered Solutions

A buffer is commonly added to each sample in analysis with the expectation that the character of the discharge will be determined largely by it and so will be little affected by variations in the extraneous composition of the samples. The data of Fig. 1 and Table II indicate that this expectation is not always realized. Whether or not a buffer is effective apparently depends on the line pairs considered and the nature of the variable extraneous material, as well as on the type and amount of buffer salt used. For example, the constancy of the Pb/Mg ratio with "small" lithium chloride additions was improved by either a sodium potassium tartrate or a potassium nitrate buffer, but that of the Cd/Mg ratio deteriorated with the larger potassium nitrate amounts at least. On the other hand, the constancy of the latter ratio was improved by either buffer when "small" calcium chloride, rather than lithium chloride, additions were made. While the use of a buffer is apparently not always a safeguard against such intensity variations, it has been found to lead to greater reproducibility in the results for any sample of constant composition.

(c) Other Results

The data of Fig. 2 indicate that the interspectra intensity ratios depend on the discharge region from which the examined radiation is emitted. Ratios associated with regions near the point and near the plane electrodes differ from each other and from that associated with radiation from the entire discharge. Moreover the three ratios are not always similarly affected by additions. Such differences might arise either from differences in the concentrations of the elements, or in excitation conditions, at different points in the discharge.

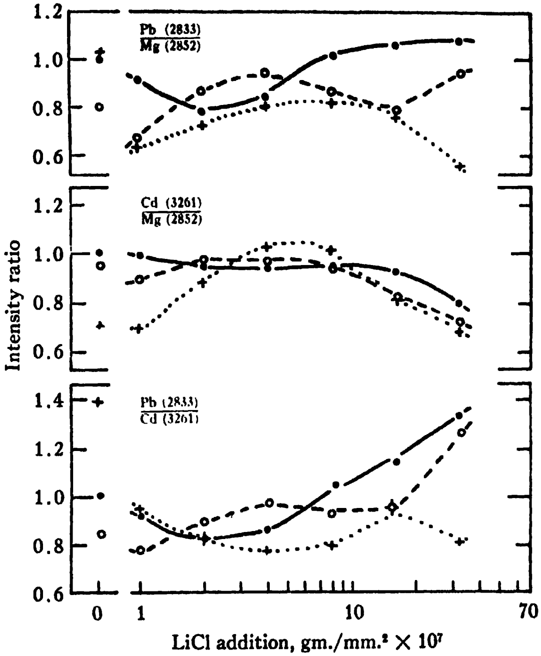


FIG. 2. *Comparison of interspectra intensity ratios in light radiated from different parts of the discharge and their dependence on the extraneous composition of the sample. The data, obtained with unbuffered samples, are for the line pairs given in Table II. The ratios for light radiated from regions on the discharge axis near the point and near the plane electrode are denoted respectively by + and O. The values for light radiated from the entire discharge are indicated b*

The data on intraspectrum intensity ratios (Fig. 3) indicate that under some conditions at least there are marked differences in the excitation conditions at different points in the discharge. These differences in excitation are apparently affected by additions to the sample. Consequently, the previous discussion is limited to the particular lines investigated.

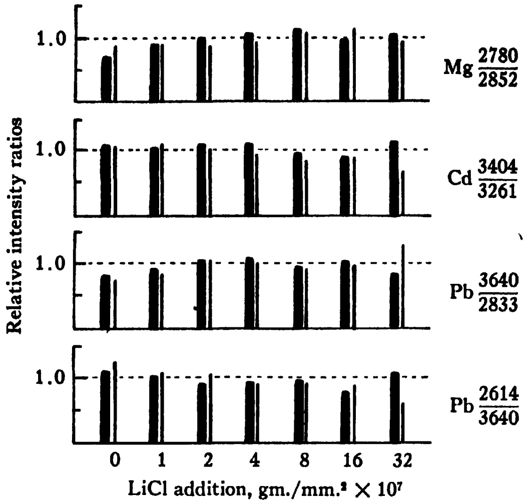


FIG. 3. *Comparison of intraspectrum intensity ratios in light radiated from different parts of the discharge, and the changes in their relative values as the extraneous composition of the unbuffered sample was altered. The ratio for light from the entire discharge has been set equal to unity for each sample, and the other ratios are given in these terms. The lengths of the light and heavy lines denote respectively the relative ratios in light radiated from regions on the discharge axis near the point and near the plane electrode.*

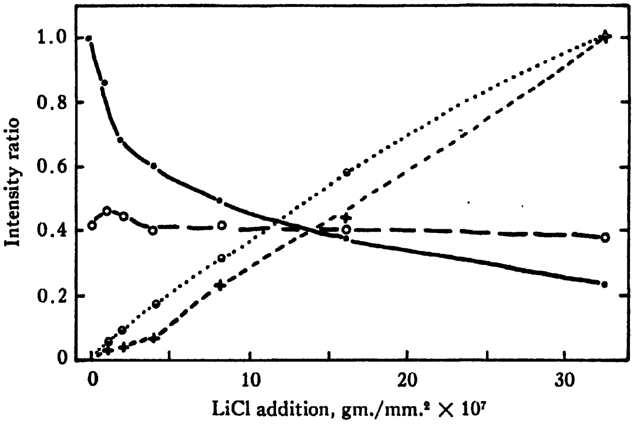


FIG. 4. *Behaviour of the intensity ratio of a line of the ionized to a line of the neutral atom spectrum on addition of extraneous material to the sample.* ● *and* ○ *denote respectively the ratios Mg II/Mg I (2937 Å/2780 Å) for unbuffered and for buffered (potassium nitrate) samples.* + *and* ⊖ *denote respectively the ratios Li I/Mg I (4603 Å/2780 Å) for the same samples, unbuffered and buffered. The latter values are plotted to give some indication of the relative amounts of lithium actually getting into the discharge for various lithium chloride additions to the sample.*

Fig. 4 shows the typical decrease that occurs in the intensity ratio of ion to neutral atom lines when additions are made to an unbuffered sample. The curve is qualitatively that expected from Saha's theory of thermal ionization (8). As applied to mixed vapours (cf. 6) theory predicts that such ratios should decrease on the addition of more easily ionized atoms to the discharge. The fact that the corresponding curve for calcium chloride additions (not presented) showed a more rapid decrease in the ratio is understandable since the Ca I/Mg I ratio showed a much steeper initial increase than the Li I/Mg I ratio, i.e., the partial pressure of Ca in the discharge increased more rapidly than that of Li in the initial stages. The virtually constant value of the Mg II/Mg I ratio obtained with the buffered sample is likewise to be expected, since the buffer supplies relatively large numbers of K atoms (ionization potential, 4.3 volts) to the discharge at all times. It may be pointed out that this interpretation of the data does not assume a decrease in the effective temperature of the discharge on addition of extraneous material; it involves consideration of partial pressures and ionization potentials only.

(d) Remarks

The observed changes in intraspectrum intensity ratios (and hence those in interspectra ratios) cannot be interpreted solely on the assumption of a decrease in "effective" discharge temperature (cf. 4). The decrease in the Mg II/Mg I ratio for the buffered sample of Fig. 4 would require a change of about 10° K in the temperature; this is far too small to account for observed changes in the ratios of lines of the neutral atom. Moreover, in some instances the changes in two different ratios require temperature changes in opposite directions.

It is doubtful that the concept of an "effective" temperature has any real meaning with respect to the details of intensity variations in these experiments. Intensity ratios in light taken from the entire discharge are results integrated over a region in which point values differ. Furthermore, they are time-integrated results. This may be an important feature when interspectra ratios are under consideration, since transport phenomena for different elements are involved. The data of this investigation have not led to any interpretation of the intensity variations in terms of source mechanisms.

References

1. Duffendack, O. S., Wiley, F. H., and Owens, J. S. Ind. Eng. Chem. Anal. Ed. 7(6) : 410-413. 1935.
2. Duffendack, O. S., Wolfe, R. A., and Smith, R. W. Ind. Eng. Chem. Anal. Ed. 5(4) : 226-229. 1933.
3. Foster, J. S., Langstroth, G. O., and McRae, D. R. Proc. Roy. Soc. (London) A, 153 : 141-152. 1935.
4. Levy, S. J. Applied Phys. 11(7) : 480-487. 1940.
5. Negresco, T. J. chim. phys. 25 : 142-153. 1928.
6. Ornstein, L. S., Brinkman, H., and Beunes, A. Z. Physik, 77 : 72-81. 1932.
7. Ornstein, L. S., Moll, W. J. H., and Burger, H. C. Objektive spektralphotometrie. Fr. Vieweg & Sohn, Braunschweig. 1932.
8. Saha, M. N. Phil. Mag. (Ser. 6) 40 : 472-488. 1920.
9. Twyman, F. and Hitchen, C. S. Proc. Roy. Soc. (London) A, 133 : 72-92. 1931.
10. Van Someren, E. H. S. J. Inst. Metals, 55 : 409-416. 1934.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. MAY, 1942 NUMBER 5

THE THEORY OF SOME A-C. COMMUTATOR MOTORS WITH SERIES CHARACTERISTICS

I. THE REPULSION MOTOR[1]

BY E. G. CULLWICK[2]

Abstract

A general method, using "full reactances", is applied for developing the theory of the simple repulsion motor, the compensated repulsion motor, and the three-phase series motor. The effect of the currents induced in the armature turns short-circuited by the brushes is included, and is shown to affect profoundly the operation of the motors. Graphical constructions for the current loci are given, together with methods of measuring the various reactances, and of accounting for the effect of saturation. Experimental results for a three-phase series motor are included and compared with calculated values.

Part I, published below, deals with the simple repulsion motor. Neglecting the effects of the coils short-circuited by the brushes, the usual well known results are obtained, and the position of the brushes for maximum starting torque is studied. The currents circulating in the coils short-circuited by the brushes are then found to have the following effects:

(*a*) The performance of the motor, for a given current, is improved at speeds below synchronism, and is impaired at speeds above synchronism.

(*b*) The maximum power factor is found to occur at some finite speed, whereas, if the effect of the short-circuited coils is neglected the power factor is a maximum at infinite speed.

(*c*) The no-load speed is considerably lower than that usually associated with series motors.

The rise and fall of the currents in the coils short-circuited by the brushes is studied in the Appendix.

List of Symbols

a, b = effective turns ratio, stator to rotor;
a, a_t = transformation ratio of transformer;
A = resultant magnetomotive force;
A_1, A_2 = magnetomotive forces, exerted by stator and rotor;
c = a constant;
e = base of natural logarithms;
e, E = e.m.f., instantaneous and r.m.s. values, in volts;
e_r, E_r = rotational e.m.f.;
e_t, E_t = transformer e.m.f.;
f = frequency of supply, cycles per second;

---

[1] *Manuscript received in original form October 28, 1941, and as revised February 9, 1942.*
Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Alta.

[2] *Professor and Head of the Department.*

i, I = current, instantaneous and r.m.s. values, in amperes;
I_1, I_2 = stator and rotor currents;
I' = yI, effective magnetizing current;
j = vector operator;
k_1, k_2 = winding coefficients, stator and rotor;
L = coefficient of self-induction;
M = coefficient of mutual induction;
N_1, N_2 = number of turns per phase, stator and rotor windings;
n = rotational speed, revolutions per second;
n_s = synchronous speed;
n_0 = minimum stable speed;
p = number of poles;
P_c = copper loss;
P_m = gross motor power, per phase, in watts;
q = pulsation;
$Q = \sqrt{2}\,Np$;
r, R = resistance, ohms;
R_1 = resistance of stator winding, per phase;
R_2 = resistance of rotor circuit, per phase;
T = torque, per phase, lb.-ft.;
T_S = starting torque, per phase;
t = time, in seconds;
V = potential difference, r.m.s. value, volts;
W = power, watts;
X = reactance, ohms;
X_1 = total reactance of stator, per phase;
X_2 = total reactance of rotor, per phase;
X_{12} = maximum mutual reactance, between stator and rotor;
x_1, x_2 = stator and rotor leakage reactance;
x_e = total equivalent leakage reactance, referred to stator;
Z = impedance, ohms;
R_e, X_e, Z_e = equivalent standstill resistance, reactance and impedance of motor, per phase;
R'_e, X'_e, Z'_e = equivalent standstill values, taking into account the effect of the short-circuited coils;
R_{et}, X_{et}, Z_{et} = total equivalent values of motor, neglecting the effect of the short-circuited coils;
R'_{et}, X'_{et}, Z'_{et} = total equivalent values, taking into account the effect of the the short-circuited coils;
R_s, X_s, Z_s = resistance, etc., of the short-circuited coil;
R_c, X_c = maximum values of the resistance and reactance of the short-circuited coils, referred to the stator;
X_{sm} = maximum mutual reactance, between stator and short-circuited coils;
X_{rm} = maximum mutual reactance, between rotor and short-circuited coils;
α, β, γ, η, θ, ψ = angles;

$y = A/A_1$;

ϕ = resultant mutual flux, in webers;

ϕ_1, ϕ_2 = mutual fluxes of I_1 and I_2;

ϕ_{L_1}, ϕ_{L_2} = leakage fluxes of I_1 and I_2;

ϕ_s = speed component of flux;

ϕ_t = transformer component of flux;

ω = pulsation of supply, $2\pi f$.

Boldface Italic type is used for quantities that are time-vectors expressed in complex notation, such as: $\boldsymbol{Z} = R + jX$. The scalar magnitude of the quantity, $\sqrt{R^2 + X^2}$, is denoted by Z.

Introduction

Much has been written on the mathematical theory of a-c. commutator motors with series characteristics, particularly in German literature, but no comparatively simple "working theory" seems to exist whereby the performance of such motors can be predetermined with a fair degree of accuracy. One of the best treatments, in the English language, of single-phase series motors is that of Steinmetz (3, pp. 499-556), who was one of the first to apply the modern methods of complex algebra to such cases. Steinmetz studied the effects of the circulating current in the coils short-circuited by the brushes, and found them to be considerable. Indeed, unless these effects and those of saturation of the iron are taken into account, a reasonable degree of accuracy in the forecasting of performance cannot be obtained.

The method to be developed in this paper has its origin in the work of Steinmetz and also in certain lectures given by Dr. C. G. Lamb, some years ago, in the Engineering School at Cambridge University.

The Repulsion Motor

1. *Fundamental Relations*

Consider a single-phase stator winding, carrying an alternating current of sinusoidal wave-form and frequency $f = \omega/2\pi$. The space-distribution of the air-gap flux-density of the magnetic field will depend on the configuration of the winding, and in all cases it may be analysed into sinusoidal harmonic components.

Suppose a single-phase rotor with a commutator rotates in the alternating magnetic field of the stator. If alternating current of the same frequency as that of the stator current is led through this rotor winding by means of brushes b and b', the stator and rotor currents will combine to set up a resultant alternating flux of amplitude ϕ. Let the angle between the flux-axis and the brush-axis be α (Figs. 1*a* and 1*b*). Confining the analysis to the fundamental component of the space-distribution of resultant air-gap flux-density, we may resolve the total flux ϕ into two components:

(1) the *speed* flux, $\phi_s = \phi \sin \alpha$, perpendicular to the brush-axis;

(2) the *transformer* flux, $\phi_t = \phi \cos \alpha$, along the brush-axis.

Adopt the convention that the sense of the rotor winding between the brushes is right-handed. Then the r.m.s. value of the e.m.f. induced between the brushes, from b to b', is

$$E_{bb'} = Q(n\phi_s + jn_s\phi_t) \tag{1}$$

in the case of Fig. 1*a*, in which the positive direction of ϕ_s is $\pi/2$ in *advance* of the positive direction of ϕ_t, and

$$E_{bb'} = Q(-n\phi_s + jn_s\phi_t) \tag{2}$$

in the case of Fig. 1*b*, in which the positive direction of ϕ_s *lags* by $\pi/2$ behind the positive direction of ϕ_t.

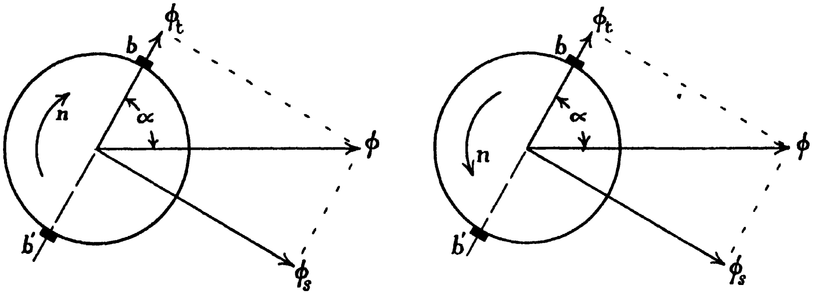


FIG. 1*a*.

FIG. 1*b*.

FIG. 1. *Speed and transformer fluxes.*

In these equations, $Q = \sqrt{2}\ Np$, where N is the number of turns in series in the rotor winding, p is the number of poles, n the rotational speed and n_s the synchronous speed; the first term of each expression, (1) and (2), is the *rotational* e.m.f., whereas the second gives the *transformer* e.m.f.*

The quantity Q is related to the reactances of the windings as follows. Suppose a current I flowing in both stator and rotor sets up a resultant mutual flux ϕ, made up of components ϕ_1 due to the stator and ϕ_2 due to the rotor windings; there will also be leakage fluxes ϕ_{L_1} and ϕ_{L_2}. Then, if $Q_1 = \sqrt{2}\ N_1p$ and $Q_2 = \sqrt{2}N_2p$:

$$Q_1n_s(\phi_1 + \phi_{L_1}) = IX_1, \tag{3}$$

$$Q_2n_s(\phi_2 + \phi_{L_2}) = IX_2, \tag{4}$$

and

$$Q_2n_s\phi_1 = Q_1n_s\phi_2 = IX_{12}, \tag{5}$$

where X_1 and X_2 are the total reactances of stator and rotor respectively, and X_{12} is the mutual reactance between the two windings.

---

* *The rotor winding is assumed to be full-pitch and uniformly distributed. For example, consider the rotational e.m.f.: this is due only to the rotational e.m.f's in bands of conductors of width* 2α *(Fig. 1a). The breadth coefficient of these bands is* $\sin\alpha/\alpha$, *and the number of turns in them is* $2\alpha N/\pi$. *Hence the rotational e.m.f. is easily seen to be* $2N\phi pn \sin\alpha \sin\omega t$, *which has an r.m.s. value* $E_r = \sqrt{2}\ Np\phi n \sin\alpha = Qn\phi_s$. *The transformer e.m.f. is obtained in a similar manner.*

Relation Between the Total and Leakage Reactances

If a is the effective turns ratio between stator and rotor, x_1 and x_2 are the leakage reactances of stator and rotor respectively, and $x_e = x_1 + a^2x_2$, the total equivalent leakage reactance of the machine referred to the stator, then it can be shown that

$$X_{12} = \sqrt{X_1X_2} - \frac{x_e}{2a} \tag{6}$$

to a very high degree of accuracy. Another form of this equation is

$$X_1X_2 \doteqdot X_{12}\left(X_{12} + \frac{x_e}{a}\right), \tag{6a}$$

since x_e is small compared with X_1, X_2, and X_{12}.

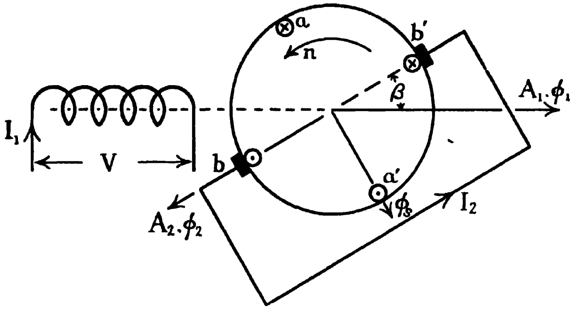


FIG. 2. *Repulsion motor.*

2. *General Theory of the Repulsion Motor*

In the simple repulsion motor shown diagrammatically in Fig. 2* the direction of rotation will be counter-clockwise; for if at the instant considered the stator magnetomotive force (m.m.f.) A_1 is from left to right, the m.m.f. A_2 of the induced armature currents must be from b' to b (i.e., it must have a component opposed to A_1) and the direction of the armature currents is downwards at a and upwards at a'. The arbitrarily chosen positive directions of the various quantities are shown by the arrows. We shall first neglect the effect of the coils short-circuited by the brushes.

The mutual flux ϕ may be resolved into stator and rotor components ϕ_1 and ϕ_2, assumed to have sinusoidal distribution in space. In addition there are the stator leakage flux ϕ_{L_1} along the stator axis and the rotor leakage flux ϕ_{L_2} along the brush axis. Resolving perpendicularly to bb', we find for the speed flux

$$\phi_s = \phi_1 \sin \beta. \tag{7}$$

The rotational e.m.f. from b' to b is, from Equation (1),

$$E_r = -Q_2n\phi_s = -X_{12}\frac{n}{n_s}I_1 \sin \beta. \tag{8}$$

It should be noted that the stator leakage flux ϕ_{L1} induces no e.m.f. in the rotor, and that the rotor leakage flux is along the brush axis and hence induces no rotational e.m.f. between the brushes. Equation (8) arises from the fact that $Q_2 n_s \phi_1$ is the transformer e.m.f. induced in the rotor, when $\beta = 0$, by the stator component of the mutual flux; i.e., it is equal to $I_1 X_{12}$, where X_{12} is the maximum mutual reactance between stator and rotor. The transformer e.m.f. from b' to b, due to the mutual flux, is

---

* *See also Fig. 8.*

$$E_{mt} = -jQ_2 n_s(\phi_2 - \phi_1 \cos\beta).$$

The rotor leakage flux ϕ_{L_2} causes an additional e.m.f. $-jQ_2 n_s \phi_{L_2}$, so that the total transformer e.m.f. is

$$E_t = -j(I_2 X_2 - I_1 X_{12} \cos\beta). \tag{9}$$

Thus, for the rotor circuit, if E is the total resultant e.m.f. due to all causes,

$$E = E_r + E_t = I_2 R_2,$$

so that, from Equations (8) and (9)

$$I_2 = -\frac{I_1\left[\frac{n}{n_s}X_{12}\sin\beta - jX_{12}\cos\beta\right]}{R_2 + jX_2} \tag{10}$$

$$= \frac{I_1}{Z_2^2}\left\{\left(X_2X_{12}\cos\beta - \frac{n}{n_s}R_2X_{12}\sin\beta\right) + j\left(R_2X_{12}\cos\beta + \frac{n}{n_s}X_2X_{12}\sin\beta\right)\right\}. \tag{11}$$

The stator terminal potential difference (p.d.) is

$$V = I_1(R_1 + jX_1) - jI_2X_{12}\cos\beta = I_1 Z_{et}, \tag{12}$$

where

$$Z_{et} = \left[R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right] + j\left[X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right] + \frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2\frac{\sin 2\beta}{2}(X_2 + jR_2), \tag{13}$$

and may be called the "total equivalent impedance". Equation (12) may be written:

$$V = I_1(R_e + jX_e) - E_r,$$

where

$$\left.\begin{aligned} R_e &= R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta, \text{ the equivalent standstill resistance,} \\ X_e &= X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta, \text{ the equivalent standstill reactance,} \\ &\text{and} \\ E_r &= -\frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2\frac{\sin 2\beta}{2}(X_2 + jR_2)I_1, \text{ the rotational e.m.f., referred to the stator.} \end{aligned}\right\} \tag{15}$$

The vector diagram is shown in Fig. 3.

The copper loss is $P_c = I_1^2 R_1 + I_2^2 R_2$. Whence, from Equation (10), the equivalent resistance of the motor when running is

$$\frac{P_c}{I_1^2} = R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\left(\cos^2\beta + \frac{n^2}{n_s^2}\sin^2\beta\right). \tag{16}$$

The gross motor power is equal to the input less the copper loss, or:

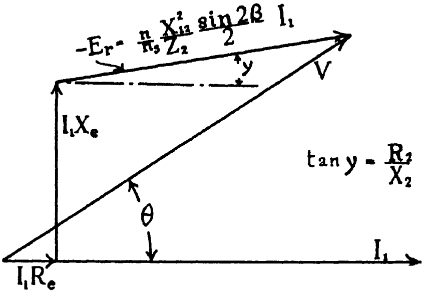

$-E_r = \frac{n}{n_s}\frac{X_{12}^2}{Z_2}\frac{\sin 2\beta}{2} I_1$
y
V
I_1X_e
$\tan y = \frac{R_2}{X_2}$
θ
I_1
I_1R_e

FIG. 3. *Repulsion motor. Vector diagram, neglecting short-circuit currents.*

$$P_m = I_1^2\frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \sin\beta\left\{X_2\cos\beta - \frac{n}{n_s}R_2\sin\beta\right\}. \tag{17}$$

The gross torque is

$$T = 0.117\frac{P_m}{n}. \tag{17a}$$

The starting torque: from Equations (12) and (17*a*), putting $n = 0$,

$$T_S = 0.117\ V^2\frac{X_2}{2n_s}\left(\frac{X_{12}}{Z_2}\right)^2 \times \frac{\sin 2\beta}{\left[R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right]^2 + \left[X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta\right]^2}. \tag{18}$$

This is a maximum, for a given *current*, when $\beta = 45°$. For a given *terminal p.d.*, if resistance is neglected the following condition for maximum starting torque is obtained by differentiation:

$$\cos^2 2\beta + \left(\frac{2X_1X_2}{X_{12}^2} - 1\right)\cos 2\beta - 2 = 0 \tag{19}$$*

If there is no leakage, this gives $\beta = 0$. Fig. 4 gives the solution of Equation (19) for different values of X_1X_2/X_{12}^2, or $1 + x_s/aX_{12}$ (See Equation (6*a*)).

3. *Rough Approximations*

If resistance and leakage are neglected ("ideal" motor), we may put $R_1 = R_2 = 0$, $X_1 = cN_1^2$, $X_2 = cN_2^2$, $X_{12} = cN_1N_2$, where c is a constant. Whence

$$Z_{st} \doteqdot X_1\sin\beta\sqrt{\left(\frac{n}{n_s}\right)^2\cos^2\beta + \sin^2\beta}. \tag{20}$$

The *power factor* is then

$$\cos\theta \doteqdot \frac{\frac{n}{n_s}\cos\beta}{\sqrt{\left(\frac{n}{n_s}\right)^2\cos^2\beta + \sin^2\beta}}, \tag{21}$$

---

* *F. W. Carter (1, p. 949) gives this result in the form:* $\tan^2\beta = \sqrt{1 - xx' + \frac{9}{4}(xx')^2} - \frac{3}{2}xx'$, *where* $x = \frac{X_{12}}{aX_1}$, $x' = \frac{aX_{12}}{X_2}$.

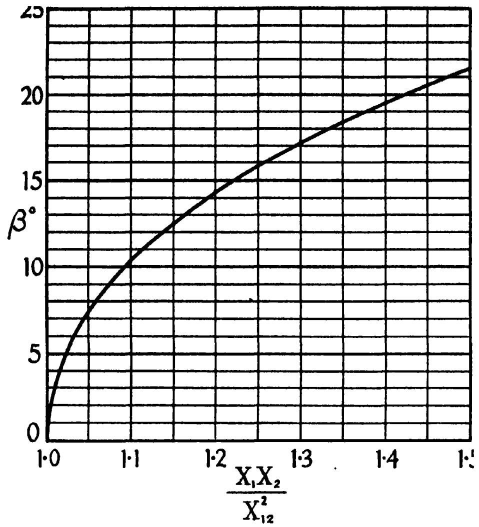


FIG. 4. *Repulsion motor. Brush-shift angle β for maximum starting torque.*

whence

$$\left(\frac{n_s}{n}\right)^2 \tan^2\beta \doteq \frac{1}{(p\,.\,f)^2} - 1. \tag{22}$$

That is, the power factor will remain approximately constant if tan β is made proportional to the speed. At synchronous speed, from Equation (21):

$$\cos\theta \doteq \cos\beta \tag{23}$$

4. *Relation Between the Transformer and Speed Fluxes, ϕ_t and ϕ_s*

If the winding coefficients of the stator and rotor windings are the same,

$$\phi_s = \phi_1 \sin\beta = KI_1N_1 \sin\beta, \tag{24}$$

where K is a constant, and

$$\phi_t = K(I_2N_2 - I_1N_1 \cos\beta). \tag{25}$$

Substituting for I_2 from Equation (11), and neglecting resistance and leakage we find that

$$\phi_t \doteq jKI_1\frac{n}{n_s}N_1 \sin\beta \doteq j\frac{n}{n_s}\phi_s. \tag{26}$$

Hence ϕ_t and ϕ_s are approximately in time quadrature. Since they are also in space quadrature it follows that they combine to form a "rotating field" whose speed is n_s in the same direction as n. At synchronous speed this rotating field is approximately constant, but at other speeds its magnitude pulsates.

5. *Commutation in the Repulsion Motor*

The commutation of a repulsion motor is inherently good at synchronous speed, a fact that may be explained either by the rotating field or, as follows, by the cancellation by the speed e.m.f. of the transformer e.m.f. induced in a coil short-circuited by a brush.

The flux ϕ_s induces a *transformer* e.m.f. in the coil (at *bb'*, Fig. 2), while ϕ_t ($= \phi_2 - \phi_1 \cos\beta$) induces a *speed* e.m.f. For the short-circuited coil, therefore, ϕ_s is the *transformer* flux and ϕ_t the *speed* flux. Since (Fig. 2) the positive direction of ϕ_t lags behind the positive direction of ϕ_s, Equation (2) applies.

The number of short-circuited coils will depend on the number of brush sets, and in the following all these coils will be treated as equivalent to one short-circuited coil whose turns are closely coupled. This approximation is equivalent to neglecting the leakage fluxes of the individual short-circuited coils.

The e.m.f. induced in the short-circuited coil by the mutual flux is therefore

$$E_s = Q_s(-n\phi_t + jn_s\phi_s) \tag{27}$$

in a direction opposed to ϕ_s, where ϕ_s is proportional to the number of turns in the coil. Now $Q_s n_s \phi_1 = I_1 X_{sm}$, where X_{sm} is the maximum mutual reactance between the stator winding and the short-circuited coil, so that from Equations (24) and (26)

$$E_s \doteqdot jI_1X_{sm}\sin\beta\left(1 - \frac{n^2}{n_s^2}\right), \tag{28}$$

which is zero at synchronous speed.

If N_s turns are short-circuited by the brushes, then, very approximately,

$$X_{sm} \doteqdot \frac{\pi N_s}{2N_2} X_{12}, \tag{29}$$

if the winding is full-pitch and uniformly distributed.

It is clear from Equation (28) that the e.m.f. in a shorted coil of a repulsion motor is small only at speeds near synchronism. At standstill and at speeds greater than about $\sqrt{2}\, n_s$ the inherent commutation is no better than that of a simple series motor.

6. *Effect of the Currents in the Short-circuited Coils on the Performance of the Repulsion Motor*

The currents induced in the short-circuited coils by the transformer effect of ϕ_s oppose the m.m.f. of the stator winding. Hence for a given value of ϕ the value of I_1 is increased. In addition, the short-circuit currents react with the transformer field ϕ_t to produce a torque whose direction depends on the speed. Since ϕ_s lags by approximately 90° in time-phase behind ϕ_t, the transformer e.m.f. in the shorted coils due to ϕ_s will be 180° out of phase with ϕ_t. That is, when ϕ_t is a maximum and in the direction *b'b*, the induced current in the shorted coil will be near its maximum value and in the direction indicated by the dotted and crossed circles near *b* and *b'* in Fig. 2. The direction of the torque due to these currents and ϕ_t is clearly in the direction of rotation, and this condition will hold provided that the quantity in brackets in Equation (28) is positive: i.e., below synchronous speed. Above synchronism, E_s reverses in sign (Equation (28)) and the commutation torque will oppose the main torque.

This effect, which tends to improve the performance below synchronism and to impair it at speeds above synchronism, is negligible in the simple series motor, since in this case the short-circuit currents and ϕ_t are nearly in time quadrature and give very little torque.

The torque due to the short-circuit currents in the repulsion motor may be calculated as follows.

The short-circuit current is, from Equation (28),

$$I_s = \frac{E_s}{R_s + jX_s} = \frac{jI_1X_{sm}\sin\beta(1 - n^2/n_s^2)(R_s - jX_s)}{Z_s^2}, \tag{30}$$

where $R_s + jX_s$ is the total impedance of the short-circuited coil, R_s being the mean value of the resistance during the commutating period. The approximation involved in assuming that this impedance is independent of the variation of the period of short-circuit with varying speed is discussed in the Appendix. In terms of X_2 we have, as a rough approximation,

$$X_s = \frac{\pi}{2}\left(\frac{N_s}{N_2}\right)^2 X_2. \tag{31}$$

This current induces an e.m.f. in the stator:

$$E_{s1} = jI_sX_{sm}\sin\beta = -I_1\left(\frac{X_{sm}}{Z_s}\right)^2\sin^2\beta(1 - n^2/n_s^2)(R_s - jX_s), \tag{32}$$

and a rotational e.m.f. E_{r1} between the brushes bb' (see Note, p. 70). Neglecting E_{r1}, the stator terminal p.d. is

$$V = I_1(R_s + jX_s) - E_r - E_{s1} = I_1Z'_{st},$$

so that the total equivalent impedance of the motor is increased by

$$Z' = \sin^2\beta(1 - n^2/n_s^2)(R_c - jX_c), \tag{33}$$

where $$X_c = X_s\left(\frac{X_{sm}}{Z_s}\right)^2 \quad \text{and} \quad R_c = R_s\left(\frac{X_{sm}}{Z_s}\right)^2. \tag{34}$$

The copper loss in the shorted coil is

$$I_s^2R_s = \frac{E_s^2}{Z_s^2}R_s = I_1^2R_c\sin^2\beta(1 - n^2/n_s^2)^2 \tag{35}$$

from Equations (28) and (34). Since the input is increased by $I_1^2R_c\sin^2\beta(1 - n^2/n_s^2)$, it follows that the *gross power* is increased by

$$P_{mc} = I_1^2R_c\sin^2\beta\frac{n^2}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right) \tag{36}$$

and the *gross torque* is increased by

$$T_c = 0.117\ I_1^2R_c\sin^2\beta\frac{n}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right). \tag{37}$$

It should be noticed that T_c is zero both at standstill and at synchronism.

We therefore have the following final results, taking into account the effect of the short-circuited coils:

The equivalent standstill resistance

$$R_s' = R_1 + R_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta + R_c\sin^2\beta. \tag{38}$$

The equivalent standstill reactance

$$X_s' = X_1 - X_2\left(\frac{X_{12}}{Z_2}\right)^2\cos^2\beta - X_c\sin^2\beta. \tag{39}$$

The rotational e.m.f. Adding the part of E_{s1} (Equation (32)) which is a function of the speed, to E_r (Equation (15)):

$$E_r' = -I_1\left\{\frac{n}{n_s}\left(\frac{X_{12}}{Z_2}\right)^2\frac{\sin 2\beta}{2}(X_2 + jR_2) - \frac{n^2}{n_s^2}\sin^2\beta(R_c - jX_c)\right\}. \tag{40}$$

The copper loss, P_c'

$$\frac{P_c'}{I_1^2} = \frac{P_c}{I_1^2} + R_c\sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right)^2, \text{ where } P_c/I_1^2 \text{ is given by Equation (16).} \tag{41}$$

The gross motor power

$$P_m' = P_m + I_1^2R_c\sin^2\beta\,\frac{n^2}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right). \tag{42}$$

The gross torque

$$T' = 0.117\,\frac{P_m'}{n}. \tag{42a}$$

Equating T' to zero gives a cubic equation for the maximum no-load speed of the motor, neglecting the rotational losses. For example, applying this to the numerical case to be worked out below, the equation is

$$\left(\frac{n}{n_s}\right)^3 - 0.785\,\frac{n}{n_s} - 4.43 = 0$$

which gives $n/n_s = 1.8$, or $n = 3240$ r.p.m.

The actual no-load speed would be less than this, on account of rotational losses. The short-circuited coils thus prevent the repulsion motor from attaining the excessively high no-load speeds which are a characteristic of series motors in general.

The total equivalent impedance

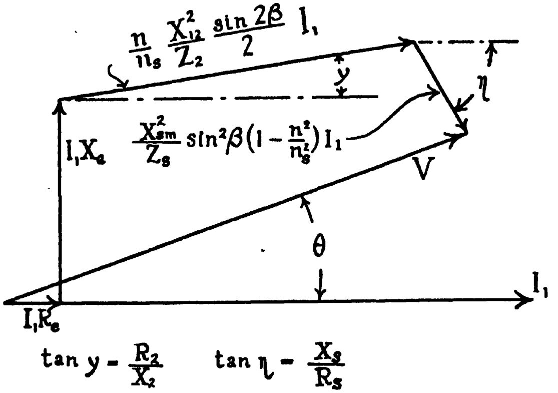
$$\begin{aligned} Z_{st}' = {} & R_s + R_c\sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right) + X_2\left(\frac{X_{12}}{Z_2}\right)^2\frac{\sin 2\beta}{2}\,\frac{n}{n_s} \\ & + j\left\{X_s - X_c\sin^2\beta\left(1 - \frac{n^2}{n_s^2}\right) + R_2\left(\frac{X_{12}}{Z_2}\right)^2\frac{\sin 2\beta}{2}\,\frac{n}{n_s}\right\}, \end{aligned} \tag{43}$$

where R_s and X_s are given by Equation (15). We may put:

$$Z_{st}' = R_{st}' + jX_{st}'. \tag{44}$$

For a given speed n, the performance may be calculated as follows: $I_1 = V/Z_{st}'$, p.f. $= \cos\theta = R_{st}'/Z_{st}'$, copper loss $= P_c'$, input $= I_1^2R_{st}'$, output $= P_m'$ − rotational losses. The gross torque is obtained from Equation (42*a*), and the starting torque by calculating I_1 for $n = 0$ and using Equation (42*a*).

The vector diagram is shown in Fig. 5.



$\frac{n}{n_s}\frac{X_{12}^2}{Z_2}\frac{\sin 2\beta}{2} I_1$
y
η
I_1X_a
$\frac{X_{sm}^2}{Z_s}\sin^2\beta(1-\frac{n^2}{n_s^2})I_1$
V
θ
I_1
I_1R_e
$\tan y = \frac{R_2}{X_2}$
$\tan \eta = \frac{X_s}{R_s}$

FIG. 5. *Repulsion motor. Vector diagram, allowing for short-circuit currents.*

7. *The Current Locus for Constant Reactances*

(*a*) *Neglecting the effect of the short-circuited coils*

To obtain the current locus by inversion we proceed as follows.

In Fig. 6 (see Equation (15)): $OX = X_e$, $XR = R_e$, $RN = -E_r/I_1$, $\tan y = R_2/X_2$. The primary current for the speed n and terminal p.d. V is then $I_1 = V/ON$, in phase and magnitude, and is represented by the vector OP passing through N.

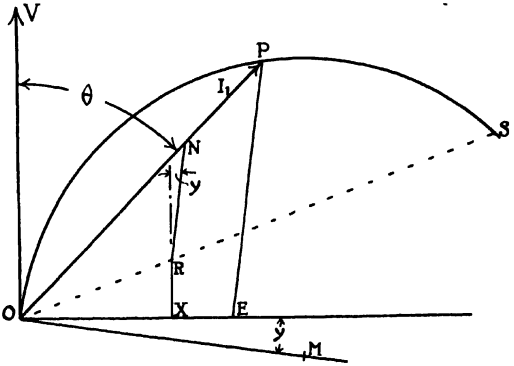


FIG. 6. *Repulsion motor. Circle diagram, neglecting short-circuit currents.*

The locus of I_1 is therefore the inverse of the line RN with respect to the origin O. This is a circle of centre M and passing through O. The standstill point is S, and the line RN or any line parallel to it may be calibrated as a speed scale.

Allowance for core loss may be made in a well known manner, but for simplicity this is omitted. The various losses and the efficiency are given by intercepts on the line *PE* parallel to *RN*.

It should be noticed that the maximum power factor occurs at infinite speed, and is equal to cos y. The effect of the short-circuited coils, however, is to make the maximum power factor occur at a finite speed, as will be seen below.

(b) Allowing for the effect of the short-circuited coils

Equation (43) may be rewritten as follows:

$$Z'_{et} = \left\{ R_e + R_c \sin^2\beta \right\} + j \left\{ X_e - X_c \sin^2\beta \right\} - \frac{E_r}{I_1} - \frac{n^2}{n_s^2} \sin^2\beta \, (R_c - jX_c), \tag{45}$$

where R_e, X_e, and E_r are given by Equation (15) and refer to the case where the effect of the short-circuited coils is neglected.

Owing to the new term in n^2, the locus of the reflected impedance is no longer a straight line, but a parabola. This parabola may be constructed from the uncorrected case as follows.

In Fig. 7, *ON* is the reflected impedance vector for the uncorrected case as in Fig. 6, and:

$$OX' = X'_e = OX - X_c \sin^2\beta, \quad X'R' = R'_e = RX + R_c \sin^2\beta.$$

OR' is thus the reflected standstill impedance vector for the corrected case, and clearly

$$\tan\eta = X_e/R_e. \tag{46}$$

Now make *R'Q* equal and parallel to *RN*. If it were not for the term in n^2 in Equation (45), *OQ* would now give the reflected impedance for the corrected case. Locate *N'* on the line *QN* so that

$$QN' = \frac{n^2}{n_s^2} Z_e \sin^2\beta. \tag{47}$$

Then *QN'* represents the last term in Equation (45), and *ON'* is the reflected impedance vector for the corrected case.

Since the correction disappears at synchronous speed, the loci of *N* and *N'* intersect at a point corresponding to synchronism. To locate *N'* for any speed:

(1) Calibrate the line *RN* as a uniform speed scale.

(2) Let the point *N* represent a speed n. From *Q* draw $QN' = \left(\frac{n}{n_s}\right)^2 R'R$.

For example, if n is $\frac{1}{2}n_s$, then $QN' = \frac{1}{4}R'R$.

In this way the parabola *R'N'* . . . is easily constructed.

The current locus is the inverse of this parabola, and may be constructed point by point by measurement. It may, however, be obtained from the uncorrected circle locus of Fig. 6 by a simple geometrical construction.

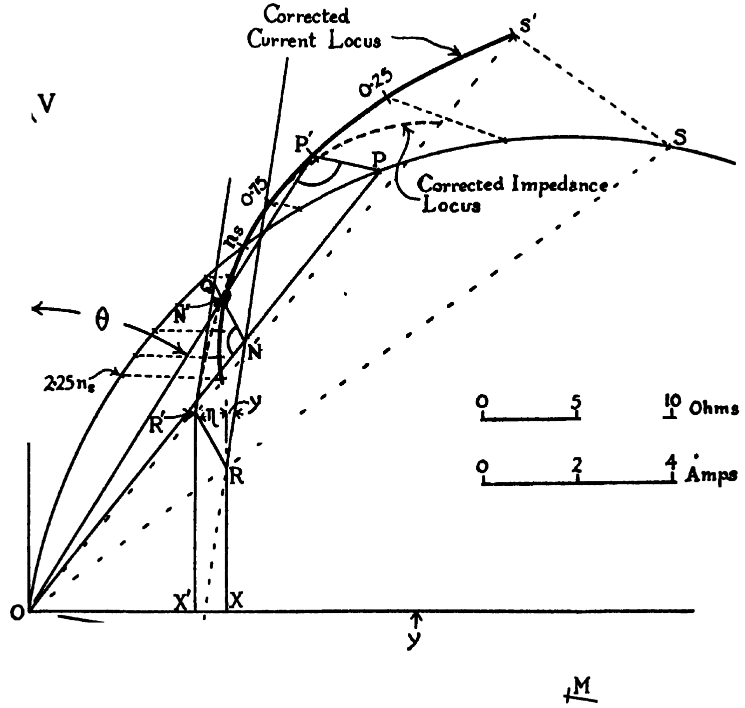


FIG. 7. *Repulsion motor. Construction of current locus, allowing for short-circuit currents.*

In Fig. 7, N and N' give the uncorrected and corrected impedances respectively for any speed n. OP is the uncorrected current vector, P lying on the circle which is the inverse of the line RN. On ON' produced locate P' such that $\angle PP'O = \angle N'NO$; then OP' is the corrected current vector, for $OP'.\,ON' = OP\,.\,ON =$ constant.

Example. Fig. 7 is drawn for the following case: $p = 4; f = 60; X_1 = 51.5; X_2 = 6.57; X_{12} = 17.4; R_1 = 1.38; R_2 = 0.98; Z_2 = 6.643; n_s = 1800$ r.p.m.; $V = 110; \beta = 18°$; h.p. $= \frac{1}{4}$; $N_2 = 144; N_s = 24$. From Equation (29) $X_{sm} \doteqdot \frac{1}{2}\pi 17.4/6 = 4.55$; from Equation (31) $X_s = \frac{1}{2}\pi 6.57/36 = 0.286$; Assuming $R_s = 0.5$ ohm, $Z_s = 0.576$, $X_c = 17.8$, $R_c = 31.2$. Then from Equation (15): $OX = 10.7$, $XR = 7.46$, $RN = \frac{n}{n_s}\,(13.24 + j\,1.97)$. From Equation (45): $OX' = 9.0$, $X'R' = 10.44$, and

$$R'N' = \frac{n}{n_s}\,(13.24 + j\,1.97) - \left(\frac{n}{n_s}\right)^2 (2.98 - j\,1.7).$$

These values can be plotted to any convenient scale. The perpendicular OT from O to the line RN is found to be 9.5 ohms, so that the diameter of the circle OP is $110/9.5 = 11.6$ amp. and its centre is on the line OT produced.

The corrected locus is shown from standstill up to $2.25\ n_s$, but the no-load speed is less than $1.8\ n_s$, as we have seen above. The maximum power factor is found to be at about 1600 r.p.m.

Thus even with constant reactances (unsaturated iron) the current locus of a repulsion motor is not a circle.

8. *Measurement of the Reactances*

The total reactances X_1, X_2, and X_{12} may be determined by simple voltmeter-ammeter tests.

The stator reactance X_1 should be measured for a range of primary current with the rotor brushes lifted, and X_1 should be plotted on a base of I_1.

The rotor reactance X_2 should be measured with the brushes down and the stator open-circuited. The coils short-circuited by the brushes have zero mutual reactance with the rotor winding, so do not affect the result. A curve of X_2 on a base of I_2 should be plotted.

To obtain the mutual reactance X_{12} the brushes should be left down and the short-circuit lead between them opened. With the brushes set at $\beta = 0$, the brush p.d. should be measured for a range of *primary* current. Again, the short-circuited coils have zero mutual reactance with the stator. X_{12} should be plotted on a base of I_1.

The equivalent leakage reactance, x_e, of the motor can be obtained by short-circuiting all the rotor coils by wrapping bare copper wire around the commutator, and by taking readings on the stator side.

The values of X_1 and X_2 are obtained approximately from the formula:

$$X = \frac{(V^2 - I^2R^2)^{\frac{1}{2}}}{I}, \tag{48}$$

where V is the p.d. across the winding, I the current, and R the resistance. Owing to core loss, the flux lags behind the current by a small angle, and Equation (48) gives the reactance of the equivalent circuit and not the true reactance. If W is the power taken, it is readily shown that the true reactance is given by

$$X = \frac{(V^2 + I^2R^2 - 2WR)^{\frac{1}{2}}}{I}, \tag{49}$$

but the two equations usually give results so nearly equal that the refinement obtained by using Equation (49) is not important.

The value of X_{12} is given by

$$X_{12} = \frac{\text{p.d. between rotor brushes}}{\text{stator current}}. \tag{50}$$

9. *The Effect of Saturation*

The reactances as obtained above will be found to vary with the current. In general they will decrease as the current increases, and in an accurate predetermination of performance the effect of this variation must be taken into account.

The simplest method of doing this is to assume some arbitrary value of the stator current I_1. The values of the reactances for the state of saturation caused by this current are substituted in Equation (43) which then gives a quadratic equation in n/n_s. The values of the reactances to be used, however, are not those that correspond directly to I_1 in the measurement of X_1, etc., since in these measurements only one winding carries current, and in actual operation the flux in the iron is a function of both stator and rotor currents, the speed, and the brush angle β.

If resistance and leakage reactance are neglected, and the stator and rotor winding factors are assumed equal, from Equation (24) :

$$\phi_s = \phi_1 \sin\beta = kA_1 \sin\beta$$

and

$$\phi_t \doteq j\frac{n}{n_s} kA_1 \sin\beta = jkA_1 \sin\beta \left(1 + \frac{n}{n_s} - 1\right),$$

where the factor k will depend on the degree of saturation, and A_1 is the m.m.f. of the stator current I_1. That is, the resultant mutual field is that due to a m.m.f. which has two components:

(1) A "rotating" m.m.f. of constant amplitude $A_1 \sin\beta$, which is directed along the brush axis when the stator current is zero.

(2) A pulsating m.m.f. directed along the brush axis of value $A_1 \sin \beta\left(\frac{n}{n_s} - 1\right)$, which is a maximum when the stator current is zero.

The resultant of these two components is a "rotating" m.m.f. whose value pulsates between $A_1 \sin\beta$ and $\frac{n}{n_s} A_1 \sin\beta$. Owing to saturation, the flux produced by this m.m.f. will have a relatively smaller pulsation. The mean amplitude of the flux will depend both on the speed and on the degree of saturation, and hence the reactances will also depend to some extent on the speed. To retain simplicity, it is necessary to ignore this effect and to assume that the mean value of the flux is that due to a m.m.f. equal to $A_1 \sin\beta$ at all speeds.

The X_1 on I_1 and X_{12} on I_1 curves plotted from the results of the measurement of X_1 and X_{12} give the reactances for a given value of I_1 when the resultant m.m.f. was equal to A_1. When the motor is operating with a current I_1 the resultant m.m.f. is roughly $A_1 \sin\beta$, and since A_1 is proportional to I_1 it follows that the average flux corresponds to that caused by a current $I_1 \sin\beta$ in the stator, with the rotor open-circuited. That is, the values of X_1 and X_{12} under running conditions are those corresponding to a current $I_1 \sin\beta$ on the X_1 on I_1 and X_{12} on I_1 curves.

The value of X_2 for a given stator current I_1 and brush angle β is that corresponding to a rotor current

$$I_2 = I_1 \frac{N_1}{N_2} \sin\beta \doteq I_1 \frac{X_1}{X_{12}} \sin\beta$$

on the graph of X_2 on I_2.

10. *To Measure* R_e and X_e

These quantities, on which depend the effect of the shorted coils, can be measured approximately as follows.

(1) With the brushes lifted, measure the stator resistance R_1 and X_1 with alternating current.

(2) With $\beta = \frac{1}{2}\pi$ and the brushes lowered, the rotor stationary, and shorting lead open, measure the stator resistance and reactance again; let these new values be R_1' and X_1'. Then, for a given current I_1, neglecting the change in reactance owing to the saturation in Case (1) being slightly different from that in Case (2), we have:

$$R_e = R_1' - R_1, \qquad X_e = X_1 - X_1' \tag{51}$$

where X_1, X_1', etc., correspond to a current $I_1 \sin \beta$.

11. *Effect of the Assumption that the Field-form is Sinusoidal*

The above theory is based on the assumption that the field-forms of both stator and rotor are sinusoidal. Actually, the distribution of conductors in a repulsion motor is that shown in Fig. 8, and results in a trapezoidal field-form for the stator and a triangular field-form for the rotor.

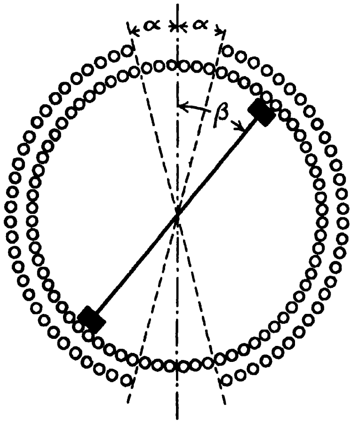


FIG. 8. *Arrangement of windings in repulsion motor. The axis of the stator winding bisects the angle 2α.*

Various workers, such as Punga (2) and Wall (4–8), have examined the effect of the distribution of the windings on the operation of the motor. Such a procedure leads to the result that the rotational e.m.f. in the rotor, and the mutually induced e.m.f's in stator and rotor, are no longer simple sine and cosine functions of the brush angle β. Wall has shown that, for a given maximum flux-density and unsaturated iron, and for values of β greater than α:

(1) The transformer e.m.f. in the rotor due to the stator current is proportional to

$$\theta_c = [\pi - 2\beta]\left[\frac{\pi^2 + 2\pi\beta - 2\beta^2 - 6\alpha^2}{\pi - 2\alpha}\right], \tag{52}$$

(2) The transformer e.m.f. in the stator due to the rotor current is proportional to

$$\theta_D = \frac{\pi^3/3 - 2\pi\alpha^2 - 2\pi\beta^2 + 4\alpha^2\beta + 4\beta^3/3}{\pi}, \tag{53}$$

(3) The rotational e.m.f. in the rotor is proportional to

$$\theta_E = \left[\frac{\pi\beta - \beta^2 - \alpha^2}{\pi - 2\alpha}\right]. \tag{54}$$

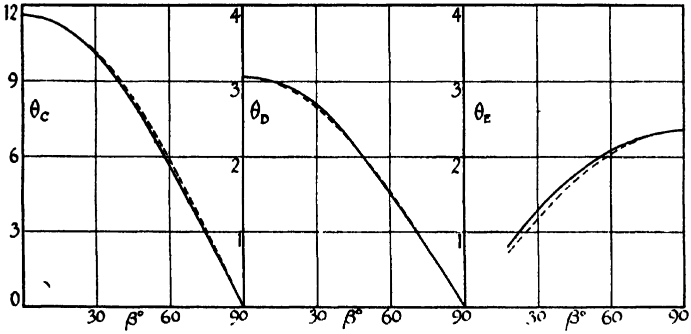


FIG. 9. *Comparison of Wall's functions and sinusoidal curves of same amplitude.* ———, *Wall's functions.* – – – – –, *Sine and cosine curves of same amplitude.*

If the field-forms are sinusoidal, the functions θ_c and θ_D are proportional to cos β, while θ_E is proportional to sin β. Wall gives graphs of these functions for the case $\alpha = 0.1\pi$, which are reproduced in Fig. 9 and compared with cosine and sine functions. It is seen that the difference between the two theories is extremely small for θ_c and θ_D, whereas in the case of θ_E (the rotational e.m.f.) the greatest difference is about 9%. In an unsaturated machine it might under certain circumstances be preferable to take the more complex expressions, but since these are based on the assumption of linear relationship between m.m.f. and flux-density it follows that in the actual case, where saturation is present, the above equations do not apply and no advantage is to be expected in using them. The assumption of sinusoidal field-forms, although not strictly rigorous, has the great advantage that the salient features of the motor's operations can be shown by means of comparatively simple formulae.

References

1. CARTER, F. W. Elec. Rev. 54 : 949. 1904.
2. PUNGA, F. Single-phase commutator motors. English translation. Whittaker and Company, London. 1906.
3. STEINMETZ, C. P. Theory and calculation of alternating current phenomena. McGraw-Hill Book Company, Inc., New York and London. 1908.

4. WALL, T. F. Electrician, 67(24) : 921-923. 1911.
5. WALL, T. F. Electrician, 67(25) : 977-980. 1911.
6. WALL, T. F. Electrician, 67(26) : 1013-1015. 1911.
7. WALL, T. F. Electrician, 68(2) : 50-52. 1911.
8. WALL, T. F. Electrician, 68(3) : 94-96. 1911.

APPENDIX

Rise and Fall of Current in the Short-circuited Coils

The impedance Z_s of the coils short-circuited by the brushes has been treated as a constant. This is equivalent to the assumption that the circulating currents are fully established at all speeds, whereas in reality as the speed increases the duration of short-circuit decreases, and owing to the time-constant of the shorted coils the circulating currents would be expected to become proportionately smaller. Theoretically, the problem is highly complex, but the simplified theory given below leads to the conclusion that the reduction of the circulating currents due to this effect is not very great.

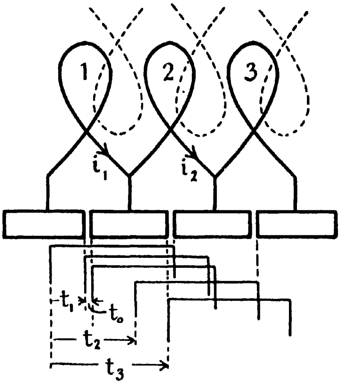


FIG. A1. *Coils undergoing short-circuit.*

Consider three adjacent armature coils, 1, 2, and 3, Fig. A1. In the position shown, coil 1 is short-circuited and the short-circuit of Coil 2 is just beginning. The brush width is taken to be greater than that of one, but less than that of two, commutator segments. Measuring time from the position shown in Fig. A1, the short-circuit of Coil 2 can be divided into five periods:

(1) From $t = 0$ to $t = t_1$, Coils 1 and 2 are both short-circuited.

(2) At time t_1 the circulating current i_1 in Coil 1 begins to break. It is arbitrarily assumed to fall to zero in a short time t_0 at a uniform rate.

(3) From $t_1 + t_0$ to t_2 Coil 2 alone carries a circulating current.

(4) At time t_2 the short-circuit of Coil 3 begins, and until time t_3 Coils 2 and 3 are both short-circuited. Clearly $t_3 - t_2 = t_1$.

(5) At time t_3 the short-circuit of Coil 2 is broken, and i_2 falls to zero in time t_0.

To simplify the analysis, it will be assumed that the resistance of the short-circuit path, R, is constant, and that the time of short-circuit is small compared with the period of the a-c. supply. The case where a constant e.m.f., E, acts in the shorted coils will therefore be analysed.

Let L be the self-inductance of each coil and M the mutual inductance with adjacent coils. L and M include the mutual effect of the coils short-circuited by the other brushes. It is assumed that the short-circuits under all brushes are synchronized; i.e., that the number of commutator segments is divisible by the number of brush sets. If this is not so, the analysis becomes very complicated.

The circulating currents i_1 and i_2 are superposed upon the ordinary load currents, which do not enter into the following analysis.

Interval $t = 0$ *to* t_1. For the growth of i_2 while i_1 is flowing:

$$E - L\frac{di_2}{dt} - M\frac{di_1}{dt} = i_2R \quad , \quad (1)$$

$$E - L\frac{di_1}{dt} - M\frac{di_2}{dt} = i_1R, \quad (2)$$

whence

$$(L^2 - M^2)\frac{d^2i_2}{dt^2} + 2RL\frac{di_2}{dt} + R^2i_2 = ER, \quad (3)$$

giving

$$i_2 = I - I(Ae^{-Rt/L+M} + Be^{-Rt/L-M}), \quad (4)$$

where $I = E/R$ and A and B are constants. Since $i_2 = 0$ when $t = 0$,

$$A + B = 1. \quad (5)$$

Also

$$i_1 = I - I(Ae^{-Rt/L+M} - Be^{-Rt/L-M}) \quad (6)$$

Interval t_0 *(*i_1 *breaks).* At t_1, the instant of break, let $i_1 = I'$ while the value of i_2 is

$$i_2' = I(1 - Ae^{-Rt_1/L+M} - Be^{-Rt_1/L-M}) \quad (7)$$

I' is assumed to fall to zero at a uniform rate in time t_0, so that during this interval

$$i_2 = I + \frac{MI'}{Rt_0} + Ce^{-Rt/L},$$

where C is a constant.

When $t = t_1$, $i_2 = i_2'$, which gives C. Thence we find that, when $t = t_1 + t_0$, i_2 has the value

$$i_2'' = I + \frac{MI'}{Rt_0}[1 - e^{-Rt_0/L}] - Ie^{-Rt_0/L}[Ae^{-Rt_1/L+M} + Be^{-Rt_1/L-M}]. \quad (8)$$

We may legitimately put $t_0 \ll L/R$, so that the second term becomes very closely equal to MI'/L, and in the third term $e^{-Rt_0/L} \doteqdot 1$. Hence

$$i_2'' \doteqdot i_2' + MI'/L. \quad (9)$$

Interval $t = t_1 + t_0$ *to* t_2. During this interval the current i_2 flows unaccompanied by any circulating current in Coils 1 or 3, so that $i_2 = I + De^{-Rt/L}$. Putting $i_2 = i_2''$ when $t = t_1 + t_0$ we find

$$i_2 = I - [I - i_2' - MI'/L]e^{-R(t-t_1-t_0)/L}. \quad (10)$$

Interval t_2 to t_3. At time t_2, Coil 3 begins its short circuit, so that the equation for i_2 must now have the same form as Equation (6), for during this interval i_2 must be identical with i_1 during the first interval t_1. That is:

$$i_2 = I - I[Ae^{-R(t-t_2)/L+M} - Be^{-R(t-t_2)/L-M}]. \tag{11}$$

But when $t = t_2$, i_2 must be given both by Equations (10) and (11). Whence, putting $B = 1 - A$ and $t_2 - t_1 - t_0 = t_s$, we find for the constants A and B:

$$A = \frac{1 + e^{-Rt_s/L}(e^{-Rt_1/L-M} - MI'/LI)}{2 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - e^{-Rt_1/L-M})} \tag{12}$$

$$B = \frac{1 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - MI'/LI)}{2 - e^{-Rt_s/L}(e^{-Rt_1/L+M} - e^{-Rt_1/L-M})}\,. \tag{13}$$

At time t_3 (where $t_3 - t_2 = t_1$) the short-circuit of Coil 2 begins to break, and at this instant i_2 must be equal to I'. Whence it is found that

$$\frac{I'}{I} = \frac{2 - (e^{-Rt_1/L+M} - e^{-Rt_1/L-M})(e^{-Rt_s/L} + 1) - 2e^{-Rt_s/L}\, e^{\frac{-Rt_1}{L-M}}\, e^{\frac{-Rt_1}{L+M}}}{2 - e^{-Rt_s/L}\left[\left(1 + \frac{M}{L}\right)e^{-Rt_1/L+M} - \left(1 - \frac{M}{L}\right)e^{-Rt_1/L-M}\right]}\,. \tag{14}$$

Substitution for I'/I in Equations (12) and (13) gives the final values of A and B, but the expressions are too unwieldy to be written down here in symbols. The best way to proceed is to take a typical numerical case. The repulsion motor cited in the paper had 48 segments. Thus at 2400 r.p.m. ($n_s = 1800$), $t_2 = 5.2 \times 10^{-4}$ sec. ($1/f = 1.67 \times 10^{-2}$ sec.). Suppose the brush width is 1.5 times the width of a segment. Then $t_1 \doteq 2.6 \times 10^{-4}$ and $t_s \doteq 2.6 \times 10^{-4}$. If $L - M$ is 3% of L: $L = 7.6 \times 10^{-4}$, $L + M = 1.5 \times 10^{-3}$, $L - M = 2.3 \times 10^{-5}$; $R = 0.5$; $M/L = 0.97$. Then

$$e^{-Rt_s/L} = 0.8428; \quad e^{-Rt_1/L+M} = 0.917; \quad e^{-Rt_1/L-M} = 0.00352.$$

Substituting these values in Equation (14), we get $I'/I = 0.6511$, whence from Equations (12) and (13):

$$A = 0.3826 \qquad B = 0.6174,$$ so that

From $t = 0$ to $t = t_1$ (Equation (4)):

$$i_2 = I[1 - 0.3826\, e^{-Rt/L+M} - 0.6174\, e^{-Rt/L-M}].$$

At t_1 (Equation 7): $\quad i_2' = 0.6470\, I.$

At $t_1 + t_0$ (Equation 9): $\quad i_2'' = 1.2786\, I.$

From $t_1 + t_0$ to t_2: $\quad i_2 = I[1 + 0.2786\, e^{-R(t-t_1-t_0)/L}]$,

so that at t_2 ($t_2 - t_1 - t_0 = t_s$):

$$i_2''' = 1.2348\, I.$$

From t_2 to t_3:

$$i_2 = I - I[0.3826\, e^{-R(t-t_2)/L+M} - 0.6174\, e^{-R(t-t_2)/L-M}],$$

and at t_3: $\quad i_2'''' = 0.6511\, I = I'.$

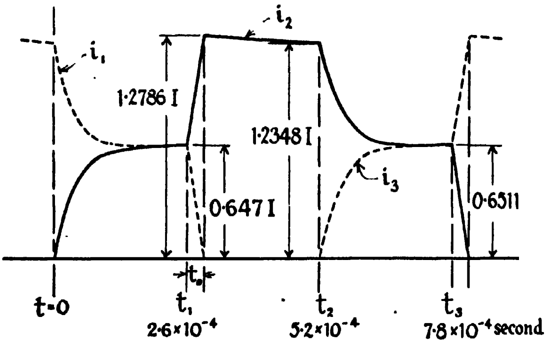


FIG. A2. *Wave forms of currents in coils short-circuited by a brush.*

The three time constants are:

$$L/R = 1.52 \times 10^{-3},\ (L - M)/R = 4.6 \times 10^{-5},\ (L + M)/R = 3 \times 10^{-3}$$

The theoretical wave-form of i_2 is shown in Fig. A.2. The average magnetizing effect of the circulating currents is that due to $i_1 + i_2 + i_3$. This has an average value of 1.2616 I. If the currents were fully established in each short-circuited coil during the whole period of short-circuit, the average circulating current would be 1.5 I. Thus in this particular case the circulating currents at 2400 r.p.m. (133% of synchronous speed) have a value only 16% less than if they were full established. Repeating the calculations for 600 and 1200 r.p.m. (one-third and two-thirds of synchronous speed), we find the decrease to be:

600 r.p.m.: 11.9% decrease
1200 r.p.m.: 13.5% decrease.

It therefore appears to be justifiable to treat Z_s, to a first approximation, as a constant.

NOTE

From Equation (30) it is seen that the rotational e.m.f. $E_{r1} = \frac{n}{n_s} X_{rm} I_s$ is proportional to $\frac{n}{n_s}\left(1 - \frac{n^2}{n_s^2}\right)$, and if included results in great complication. Fortunately the effect is zero both at standstill and at synchronism, and is small at intermediate speeds. Since repulsion motors are not usually designed to run at speeds much above synchronism, this effect is neglected in comparison with E_{s1}. Thus no error is introduced in the results for the starting conditions, which are affected profoundly by the transformer e.m.f. E_{s1}, and very little error over the normal speed range of the motor. This approximation has the great advantage of enabling us to retain the practicability of a graphical construction, which is so valuable in giving a general picture of the behaviour of a machine. For accurate design work, the effect can be included, and the reader is referred to a recent paper by P. H. Trickey (Trans., Am. Inst. Elect. Engrs. 60(2) : 67-72. 1941.)

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. A. JUNE, 1942 NUMBER 6

BAND SPECTRUM AND STRUCTURE OF THE CH$^+$ MOLECULE; IDENTIFICATION OF THREE INTERSTELLAR LINES[1]

By A. E. Douglas[2] and G. Herzberg[3]

Abstract

In a discharge through helium, to which a small trace of benzene vapour is added, a new band system of the type $^1\Pi - {}^1\Sigma$ is found which is shown to be due to the CH$^+$ molecule. The $R(0)$ lines of the 0–0, 1–0, and 2–0 bands of the new system agree exactly with the hitherto unidentified interstellar lines 4232.58, 3957.72, 3745.33 Å, thus proving that CH$^+$ is present in interstellar space. At the same time this observation of the band system in absorption shows that the lower state $^1\Sigma$ is the ground state of the CH$^+$ molecule. The new bands are closely analogous to the $^1\Pi - {}^1\Sigma^+$ BH bands. The analysis of the bands leads to the following vibrational and rotational constants of CH$^+$ in its ground state: $\Delta G_{\frac{1}{2}}'' = 2739.54$, $B_e'' = 14.1767$, $\alpha_e'' = 0.4898$ cm.$^{-1}$. The internuclear distance is $r_e'' = 1.1310 \cdot 10^{-8}$ cm. (for further molecular constants see Table V). From the vibrational levels of the upper $^1\Pi$ state the heat of dissociation of CH$^+$ can be obtained within fairly narrow limits: $D_0(\mathrm{CH}^+) = 3.61 \pm 0.22$ e.v. From this value the ionization potential of CH is derived to be $I(\mathrm{CH}) = 11.13 \pm 0.22$ e.v. The bearing of this value on recent work on ionization and dissociation of polyatomic molecules by electron impacts is briefly discussed.

A. Introduction

The work of Swings and Rosenfeld (22) and McKellar (14, 15, 16) has shown definitely that certain interstellar lines found by Dunham and Adams (6, 5, 1) are due to the absorption by CH and CN (and possibly NaH) molecules present in interstellar space. Since these interstellar molecules are practically undisturbed by collisions with other molecules or atoms, if they have once been excited they will radiate all their energy and in general go over into the very lowest state (electronic, vibrational, and rotational) before they will absorb another quantum. That is why only single sharp lines, rather than bands, are observed which agree with those lines of the laboratory bands that have the lowest (or in two cases the second lowest) rotational and vibrational level of the ground state as their lower state.

Apart from the mysterious diffuse interstellar bands found by Merrill and Wilson (17, 18) and Beals and Blanchet (3) four sharp interstellar lines 3579.04, 3745.33, 3957.72, 4232.58 Å remained unexplained. Since they could hardly be atomic in origin and since they fitted none of the absorption

---

[1] *Manuscript received February 26, 1942.*

Contribution from the Department of Physics, University of Saskatchewan, Saskatoon, Sask., with financial assistance from the National Research Council of Canada

[2] *Physicist, National Research Laboratories, Ottawa.*

[3] *Research Professor of Physics.*

spectra of known molecules, as has been carefully checked by McKellar (16)*, Swings† at a recent conference held at the Yerkes Observatory suggested that they might be due to some molecular ion such as CN^+, CH^+, NO^+ . . . . while Mulliken† suggested the CH_2 molecule. For a number of reasons which need not be given here, Teller and Herzberg‡ concluded that of these possibilities CH^+ was the most likely one. However, at the time, no spectrum of any of the suggested molecules was known.

We therefore thought it worth while to try to find a spectrum of CH^+. In what follows we report the observation of such a spectrum to which three of the four interstellar lines mentioned above belong. Thus these interstellar lines have been definitely identified and information about the structure of the CH^+ molecule has been obtained [compare our preliminary note (4)].

B. Experimental

The new bands here to be discussed were first found in the spectrum of an electrodeless discharge through helium mixed with a small trace of benzene vapour and excited by a powerful high frequency oscillator. However, it was soon found that an ordinary uncondensed discharge with electrodes constitutes an equally good or even better source. Fig. 1 shows relevant parts of the spectrum of the latter source obtained with the Saskatoon 6 m. grating. It may be mentioned that the spectrograms were taken when the colour of the discharge was almost wholly that characteristic of helium. The Swan bands of C_2, which on first admitting the benzene to the helium are very strong, were comparatively weak when the spectra were taken. On the other hand, the CH bands occur very strongly on the spectrograms. The exposure time for the stronger bands was only about one hour, while, for the weaker bands, exposures up to 10 hr. were necessary.

The measurements, mostly of second order plates, were made with a Gaertner comparator. The absolute accuracy of the wave-lengths (referred to iron standards) is estimated to be better than ± 0.01 Å, while the relative accuracy is probably ± 0.003 Å or better.

C. Band Analysis

The rotational and vibrational analysis of the new bands did not offer any difficulty. All the bands are shaded to the red. Each band, as shown by Fig. 1, consists of three branches which are readily identified as P, Q, and R branches. Of these the P branch is the weakest. Unless there is some unresolved fine structure the band system must therefore represent a $^1\Pi - {}^1\Sigma$ or a $^1\Sigma - {}^1\Pi$ transition. The fact that the line $R(0)$ is present while $P(1)$ is absent shows that the transition is $^1\Pi - {}^1\Sigma$, and at the same time

---

* *We are greatly indebted to Dr. McKellar for sending us a copy of his paper in advance of publication.*

† *Paper at conference on interstellar lines, held at the Yerkes Observatory in June 1941; see the summary by Ledoux (12).*

‡ *Discussion at the Yerkes Conference; see Ledoux (12).*

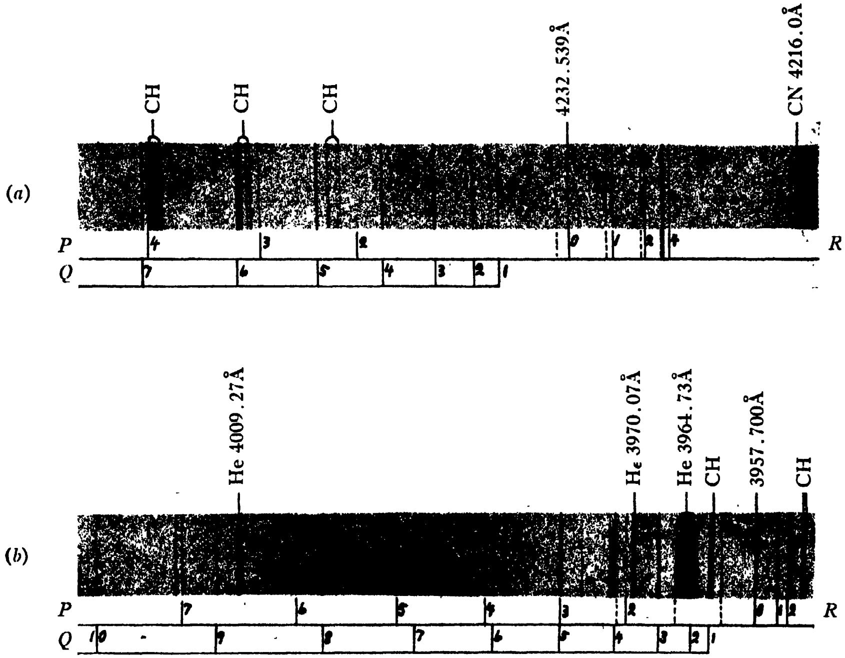


FIG. 1. CH⁺ *bands, (a) 0–0 band, (b) 1–0 band. The broken leading lines refer to lines of the returning part of the R branch.*

excludes the possibility $^1\Pi - {}^1\Delta$ or $^1\Delta - {}^1\Pi$ which, except for more missing lines near the origin, would give a similar structure if the Λ doubling is small. A multiplet $\Pi - \Sigma$ transition would have the same structure as observed if the multiplet splitting were unresolved. However, as far as we are aware, no multiplet $\Pi - \Sigma$ bands of molecules other than H_2 or He_2 are known which under such a high dispersion as used here show no splitting. Therefore we consider it as proved that the new bands are $^1\Pi - {}^1\Sigma$ bands.

TABLE I

DESLANDRES TABLE OF THE CH^+ BANDS

ν_0 = wave number of zero line
ν_H = wave number of band head (R branch)

v' \ v''	0	1
0	ν_0 = 23596.94 cm.$^{-1}$ ν_H = 23660.52	ν_0 = 20857.40 cm.$^{-1}$ ν_H = 20932.72
1	ν_0 = 25239.10 ν_H = 25281.35	*
2	ν_0 = 26673.40 ν_H = 26704.14	

* *The 1–1 band appears faintly on a number of plates but it was too weak and too strongly overlapped to be measured.*

In Table I a Deslandres table of the observed bands is given. In spite of a good deal of effort we have been unable to extend the band system further. We tried particularly to find the 3–0 band since it appeared likely that the fourth hitherto unidentified interstellar line λ3579.04 belongs to this band. However, with our source there occur in the same region the $\Delta v = 1$ sequences of the Deslandres-d'Azambuja bands of C_2 and of the violet CN bands consisting of a large number of lines which make an unambiguous identification of a weak CH^+ band impossible. Neither have we been able to find the 3–1 band (which would be sufficient to fix the position of the $v' = 3$ level) even though its expected position is in a more favourable spectral region.

In Table II are given the wave numbers of all the band lines of the CH^+ system with the assignment of the J values. None of the bands extends to very high J values. The J values are also indicated on the spectrograms of the 0–0 and 1–0 bands in Fig. 1, where it is seen that the numbering chosen is obvious. Table III gives the combination differences $\Delta_2F''(J)$ for the 0–0, 1–0, and 2–0 bands which agree very satisfactorily. On the other hand, there is a systematic difference between the $\Delta_1F'(J)$ values calculated from $R(J) - Q(J)$ and those calculated from $Q(J+1) - P(J+1)$ of each band, indicating a not negligible Λ type doubling in the upper $^1\Pi$ state. The rotational constants for the upper levels of the Q branches were therefore evaluated independently from those of the P and R branches.

TABLE II

WAVE NUMBERS OF BAND LINES

J	0–0 Band			1–0 Band			2–0 Band			0–1 Band*		
	R(J)	*Q(J)*	*P(J)*	*R(J)*	*Q(J)*	*P(J)*	*R(J)*	*Q(J)*	*P(J)*	*R(J)*	*Q(J)*	*P(J)*
0	23619.85			25259.97			26692.50			20880.27		
1	637.71	23591.89		274.22	25232.20		702.76	26664.57		899.13	20853.31	
2	650.48	581.77	23536.26	281.35	218.28	25176.62	704.14	646.91	26608.99	913.83	845.18	20799.88
3	658.14	566.56	498.57	281.35	197.43	135.10	696.61	620.41	563.69	924.37	832.88	764.90
4	660.52	546.23	455.87	274.22	169.54	086.80	679.95	584.88	509.67	930.77	816.50	726.24
5	657.55	520.70	408.37	259.97	134.50	031.62	654.10	540.36	446.89	932.72	795.85	683.39
6	649.10	489.92		237.93	092.35	24969.61	618.86	486.79	375.35	930.08	770.87	636.84
7	635.01	453.76		208.57	042.86	900.63	574.17	423.95	294.96		741.57	
8		412.16		171.36	24985.95	824.68	519.77	351.82	205.56		707.73	
9				126.22	921.48			270.18				
10					849.28			178.85				
11					769.27							

* *This band was measured on a first order spectrogram. The wave numbers are therefore somewhat less accurate than those of the other bands which were measured on second order spectrograms.*

TABLE III

COMBINATION DIFFERENCES $\Delta_2F''(J)$ FOR THE 0–0, 1–0, AND 2–0 BANDS

J	$\Delta_2F''(J) = R(J-1) - P(J+1)$		
	0–0 Band	1–0 Band	2–0 Band
1	83.59	83.35	83.51
2	139.14	139.12	139.07
3	194.61	194.55	194.47
4	249.77	249.73	249.72
5		304.61	304.60
6		359.34	359.14
7		413.25	413.30

D. Rotational and Vibrational Constants

In Table IV the rotational constants B_v and D_v, as calculated from the observed bands, are given. The constants B_0'' and D_0'' were obtained in the usual way [see Herzberg (9)] from the average of the $\Delta_2F''(J)$ values given in Table III. The B and D values for the upper states of the Q branches B_v^Q and D_v^Q were obtained by determining $B' - B''$ and $D' - D''$ from the plot $Q(J)$ against $J(J+1)$ and assuming the B_0'' and D_0'' value obtained before. This same method also yielded B_1''. The B and D values for the upper states of the P and R branches B_v^{PR} and D_v^{PR} were obtained both from the $\Delta_2F'(J) = R(J) - P(J)$ and by plotting* $R(J-1) + P(J)$ against J^2. The values given in Table IV are the averages of the values obtained in the two ways.

TABLE IV

ROTATIONAL CONSTANTS OF CH^+

v	Upper state, $^1\Pi$				Ground state, $^1\Sigma^+$	
	B_v^Q, cm.$^{-1}$	B_v^{PR}, cm.$^{-1}$	B_v^{average}, cm.$^{-1}$	D_v^{average}, cm.$^{-1}$	B_v'', cm.$^{-1}$	D_v'', cm.$^{-1}$
0	11.4088	11.4482	11.4285	0.00199	13.9318	0.00139
1	10.4691	10.5010	10.4850	0.00211	13.4420	0.00136
2	9.5206	9.5488	9.5347	0.00214		

As is well-known, for $^1\Pi$ states the Λ type doubling is given by

$$\Delta\nu_{dc}(J) = qJ(J+1) \tag{1}$$

where q is the difference between the B_v^Q and the B_v^{PR} values. This difference is quite appreciable in the present case. We have for $v' = 0$: $q_0 = 0.0394$ cm.$^{-1}$, for $v' = 1$: $q_1 = 0.0319$ cm.$^{-1}$, and for $v' = 2$: $q_2 = 0.0282$ cm.$^{-1}$. Thus q decreases with increasing v'. It is significant that $B_v^{PR} > B_v^Q$, as would be expected if the splitting is produced by the interaction of the $^1\Pi$ state with the lower $^1\Sigma^+$ state.

---

* *It may be noticed that a misprint occurs in Herzberg (9, p. 204): The D correction is not* $-2(D' - D'')J^2(J+1)^2$ *but* $-2(D' - D'')J^2(J^2+1)$.

Since the D_v^Q and D_v^{PR} values for the $^1\Pi$ state were found to be the same within the accuracy of the determinations only their average values are given in Table IV.

For the ground state the available data do not allow any conclusions about a possible curvature of the B_v versus v curve. In the upper state the B_v^Q, the B_v^{PR}, as well as the average B_v values show definitely the presence of a negative quadratic term in the formula

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2. \qquad (2)$$

The B_e'', α_e'', B_e', α_e', γ_e' values obtained from the B_v'' and $B_v'^{(\text{average})}$ are given together with other constants in Table V. Assuming that the emitter of the bands is CH^+ (see Section *E*) we obtain from the B_e values the internuclear distances r_e, also given in Table V.

For the lower state only the first vibrational quantum $\Delta G_{\frac{1}{2}}''$ but not ω_e'' and $\omega_e''x_e''$ can be obtained. For the upper state the values of ω_e' and $\omega_e'x_e'$ resulting from the zero lines in Table I are given in Table V.

TABLE V

MOLECULAR CONSTANTS OF CH^+

	Upper state, $^1\Pi$	Ground state, $^1\Sigma^+$
B_e, cm.$^{-1}$	11.8977	14.1767
B_0, cm.$^{-1}$	11.4285	13.9318
α_e, cm.$^{-1}$	+0.9367	+0.4898
γ_e, cm.$^{-1}$	−0.0034	—
D_e, cm.$^{-1}$	0.00195	0.00141
β_e, cm.$^{-1}$	+0.00008	−0.00003
I_e, gm.-cm.^{2}[*]	$2.3529 \cdot 10^{-40}$	$1.9746 \cdot 10^{-40}$
r_e, cm.[*]	$1.2345 \cdot 10^{-8}$	$1.1310 \cdot 10^{-8}$
r_0, cm.[*]	$1.2596 \cdot 10^{-8}$	$1.1409 \cdot 10^{-8}$
ω_e, cm.$^{-1}$	1850.02	$\Delta G_{\frac{1}{2}}$ = 2739.54
$\omega_e x_e$, cm.$^{-1}$	103.93	—
$\nu(0, 0)$, cm.$^{-1}$	23596.94	—

[*] *These values have been obtained from the B values with the conversion factors given by Herzberg (9).*

E. Nature of Band Emitter

The values of the rotational constants *B* found above from the fine structure of the new bands, if compared with the *B* values of other diatomic molecules, prove unambiguously that the emitter must be a neutral or ionized hydride molecule of an element between Li and F[*]. The fact that the bands appear in interstellar absorption (see section *F*) shows conclusively that their lower $^1\Sigma$

---

[*] *Going to extremes one might also consider SH and HCl, but they can also be eliminated in much the same way as shown below for all but one of the hydrides of Li to F.*

state must be the ground state of the molecule. The ground states of the molecules LiH, BeH, BeH$^+$, BH, BH$^+$, CH, NH, OH, OH$^+$, HF are known [see Table 36 in Herzberg (9)], but their B_e, B_0 and $\Delta G_{\frac{1}{2}}$ values do not agree with those observed for the lower state of the new bands. Therefore only the ionized molecules LiH$^+$, CH$^+$, NH$^+$, HF$^+$ remain to be considered as possible emitters of the new bands. However, of these four molecules only CH$^+$ (as it has an even number of electrons) can have singlet states. Since the new bands are definitely singlet bands we conclude that they are due to the CH$^+$ molecule. This conclusion appears inevitable except for the remote possibility of a doubly ionized hydride molecule as the emitter. However, this appears extremely unlikely and will be definitely excluded below.

We have purposely refrained, in the above proof, from making use of arguments based on the conditions of excitation, since in the past many wrong identifications have been made on this basis. However, it is gratifying that the identification of the emitter as CH$^+$ is exceedingly plausible from the point of view of the conditions of excitation. One would expect in discharges of the type described above mainly bands due to C_2 and CH and the corresponding ionized molecules, and from the singlet structure of the bands and the B values one would immediately conclude that the emitter must be CH$^+$ (CH and CH^{++} have no singlet states). To be sure, CN and NH bands appeared as impurities. While the new bands certainly do not belong to NH, whose spectrum is known, nor to NH$^+$, which would have doublet bands, NH^{++}, although exceedingly unlikely, cannot immediately be excluded on this basis (see however below).

It is well known that the r_e'' values of the neutral diatomic hydrides of each period of the periodic system form a fairly smooth curve if plotted against the atomic number [see Fig. 180 of reference (9)]. The same would be expected for the ionized hydrides. In Fig. 2, instead of the r_e'' values, the B_e'' values are plotted against the number of outer electrons since the B_e values do not involve any assumption about the atomic masses. It is seen that the B_e'' value of the new bands fits exceedingly well into the curve for the ionized hydrides if CH$^+$ is taken to be the emitter. This would also exclude the molecules LiH$^+$, NH$^+$, and HF$^+$ if they were not already excluded on the basis of the previous argument. But in addition this diagram excludes also the possibility (left open above) of a doubly ionized molecule. The B values of the doubly ionized hydrides would lie on a third curve whose approximate position is indicated by a dotted line in Fig. 2. The only doubly ionized hydride molecule that would exhibit a $^1\Pi - {}^1\Sigma$ system as a resonance transition would be NH^{++}. Even considering the uncertainty of the dotted curve in Fig. 2, it appears certain that $B(\text{NH}^{++})$ would be larger than the observed B_e'' for the new bands. In other words, NH^{++} cannot be the emitter of the bands. Indeed it would have been hard to understand an excitation of bands of a doubly ionized molecule in a discharge in which the excitation is essentially by means of metastable He atoms of 19.7 e.v. energy.

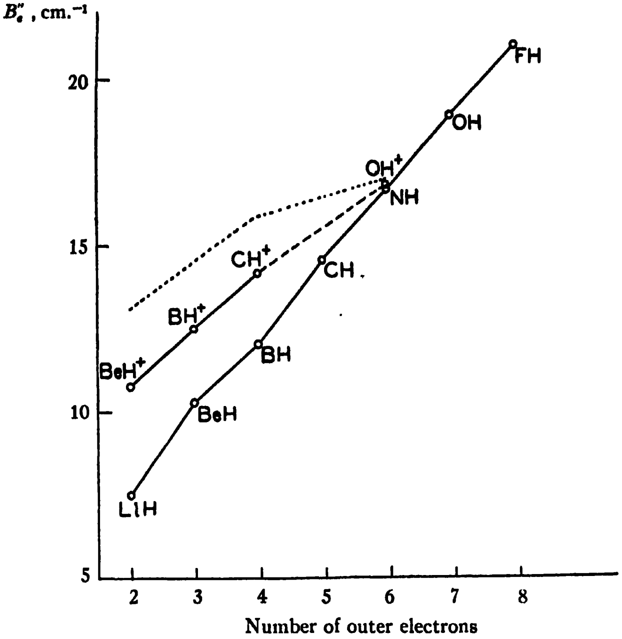


FIG. 2. *B_e'' values of neutral and ionized diatomic hydrides.*

A further proof, if such is necessary, that the new bands are due to CH^+ is the close analogy to the $^1\Pi - {}^1\Sigma^+$ bands of the BH molecule, which has the same number of electrons. The electronic excitation energy $\nu_{00} = 23596.94$ is very similar in magnitude to that of BH which is $\nu_{00} = 23073.9$. The constant q_0 of the Λ-type doubling in the $^1\Pi$ state of BH is $q_0 = 0.0337$ cm^{-1}. [see Thunberg (23)] while for CH^+ (see above) it is 0.0394. Also for both molecules $q_1 < q_0$. In both cases the q_0 values deviate in the same direction from those calculated on the assumption of pure precession [$q_0^{\text{calc.}}$ (BH) = 0.049 cm.$^{-1}$, $q_0^{\text{calc.}}$ (CH^+) = 0.044 cm.$^{-1}$, see Mulliken and Christy (19)].

Finally it is significant that the values of the internuclear distance vibrational frequency, and dissociation energy (see below) in the ground state of the emitter of the new bands ($r_e'' = 1.1310 \cdot 10^{-8}$cm., $\Delta G_{\frac{1}{2}}'' = 2739.54$, $D_0 = 3.61 \pm 0.22$ e.v.) are very close to the corresponding values of neutral CH ($r_e'' = 1.1201$, $\Delta G_{\frac{1}{2}}'' = 2732$ cm.$^{-1}$, $D_0 = 3.47 \pm 0.02$ e.v.). This is just what would be expected for CH^+ since the most loosely bound electron in CH which is removed in CH^+ is a distinctly non-bonding electron.

Recently Gerö and Schmid (7, 8) have reinvestigated certain ultraviolet bands originally discovered by McDonald (13) and have tentatively ascribed them to CH^+. Their conclusion as to the emitter of their bands appears to be far less certain than the conclusions concerning our bands. At any rate the vibrational quanta of the upper and lower states of their bands do not agree with those of our bands. If their bands are due to CH$^+$ they must correspond to a transition between two fairly highly excited electronic states. Under the conditions of excitation used by us the McDonald–Gerö–Schmid bands do not occur, at least not sufficiently strongly to appear on our plates. It would be interesting to know whether our bands occur under their conditions of excitation. From the fact that they used a condensed discharge and also from the observed structure of their bands it does not appear to be impossible that their bands are due to CH^{++} (a $^2\Sigma - {}^2\Sigma$ transition would be expected for CH^{++} in about the region where these bands occur).

F. Dissociation Energy of CH$^+$, Ionization Potential of CH and Related Questions

The vibrational quanta of the upper state $^1\Pi$ of the CH$^+$ bands converge rather rapidly. A linear extrapolation gives for the dissociation energy $D_0(^1\Pi) = 7350$ cm.$^{-1}$, a value that is only twice as high above $v' = 0$ as the energy of the last observed vibrational level ($v' = 2$). According to the experience with other diatomic molecules the above value should at any rate represent an upper limit for $D_0(^1\Pi)$. On the other hand, the failure to observe bands with $v' > 2$ suggests that $v' = 2$ is the last vibrational level, or that higher levels are unstable in consequence of predissociation into another electronic state. The latter possibility can be excluded since there is only one dissociation limit in the energy range considered (see also further below). But it is entirely possible that the vibrational levels of the $^1\Pi$ state converge much faster than linearly and that in consequence of that $v' = 2$ is the last vibrational level. In this case $D_0(^1\Pi)$ would be somewhere between the last observed and the first extrapolated level ($v' = 3$), that is, equal to about 3700 cm.$^{-1}$. This value must be considered as a *lower* limit* for $D_0(^1\Pi)$. In the following we shall use the mean of the two limiting values, that is, $D_0(^1\Pi) = 5500$ cm.$^{-1}$ where the error cannot be more than ± 1800 cm.$^{-1}$. Adding D_0 ($^1\Pi$) to the electronic excitation energy 23597 cm.$^{-1}$ we obtain for the dissociation limit of the $^1\Pi$ state $E_d(^1\Pi) = 29100 \pm 1800$ cm.$^{-1}$ $= 3.61 \pm 0.22$ e.v. above the ground state. In order to obtain from this value the dissociation energy of CH$^+$ we have to know the excitation energy of the products of dissociation. The lowest state of the products is C$^+(^2P)$ + H(^2S). The next two higher states are C(^3P) + H$^+(^1S)$ and C(^1D) + H$^+(^1S)$, which are 2.331 and 3.594 e.v. above the lowest state. The upper $^1\Pi$ state of the CH$^+$ bands cannot result from C(^3P) + H$^+(^1S)$ according to the Wigner-Witmer correlation rules ($^3P + {}^1S$ gives only triplet states). If it resulted from C(^1D) + H$^+(^1S)$ the dissociation energy of the ground state $^1\Sigma^+$ into C$^+(^2P)$ + H(^2S) would have to be $3.61 - 3.59 = 0.02 \pm 0.22$ e.v., which is impossible. Therefore we conclude that both states $^1\Sigma^+$ and $^1\Pi$ dissociate into $C^+(^2P) + H(^2S)$ and that the dissociation energy of CH^+ is

---

* *If the potential curve had a maximum it would be only an upper limit. However, even though the $^1\Pi$ state of BH has a maximum [see Herzberg and Mundie (10)] it appears very likely, on account of the much greater r_e' value, that for CH$^+$ a maximum, if it exists, has only a very small height.*

$$D_0(CH^+) = 3.61 \pm 0.22 \text{ e.v.}$$

From the relation

$$I(CH) + D(CH^+) = D(CH) + I(C), \qquad (3)$$

where $I(CH)$ and $I(C)$ are the ionization potentials of CH and C, respectively, one obtains, with the above value of $D(CH^+)$ and with $D(CH) = 3.47$ e.v. [see Herzberg (9)] and $I(C) = 11.267$ e.v. [see Bacher and Goudsmit (2)],

$$I(CH) = 11.13 \pm 0.22 \text{ e.v.}$$

A few years ago Smith (20) observed the appearance potential of CH^+ ions when CH_4 is bombarded with electrons of varying velocities and from it obtained two upper limits for the ionization potential of CH, $I(CH) \leqslant 11.7$ or $\leqslant 16.2$ e.v. depending on whether the mechanism for the formation of CH^+ is assumed to be $CH_4 \rightarrow CH^+ + 3H$ or $CH^+ + H_2 + H$. Later Kusch, Hustrulid, and Tate (11) from a similar study of HCN obtained an upper limit $I(CH) \leqslant 15.4$ e.v. and concluded that for CH_4 the process by which CH^+ is formed is $CH_4 \rightarrow CH^+ + H_2 + H$, since otherwise the CH^+ ions formed in the dissociation of HCN would have to have a kinetic (or vibrational) energy of at least 3.7 e.v. at the appearance potential.

Our spectroscopic value for $I(CH)$ reverses this conclusion, showing that at the appearance potential of CH^+ in HCN the products of dissociation do have an "excess" energy as high as 4.3 e.v. This result is of importance because in most discussions of the results of electron impact experiments on polyatomic molecules it has been assumed that the excess energy at the appearance potential of a certain ion is always small and certain energetically possible dissociation processes have been eliminated because they would involve fairly large "excess" energies. On the basis of the above result it is now, for example, no longer possible to exclude one of the dissociation processes $CH_4 \rightarrow CH^+ + 3H$ or $CH_4 \rightarrow CH^+ + H_2 + H$ even though the latter involves an excess energy of 5.3 e.v. at the appearance potential. It is of course not necessary to assume that all the excess energy is kinetic energy of translation. It may be also vibrational or electronic excitation energy of the products of dissociation. On the basis of the potential hyperfaces it is easy to visualize qualitatively that two competing processes may start in at one and the same energy of the bombarding electrons. It may be mentioned that even without the knowledge of the CH^+ spectrum one could have eliminated the suggested values $I(CH^+) = 16.2$ or 15.4 e.v., since on the basis of the above cycle (3) they would imply negative $D(CH^+)$ values (-1.5 and -0.7 e.v. respectively).

G. Identification of Interstellar Lines

It was mentioned in the introduction that in the case of light molecules almost exclusively the transitions from the lowest rotational level of the electronic and vibrational ground state occur in interstellar absorption.

For a $^1\Pi - {}^1\Sigma$ transition these would be the $R(0)$ lines. In Table VI the wave-lengths of the $R(0)$ lines of the 0–0, 1–0, and 2–0 CH+ bands as observed in the laboratory, and also the observed wave-lengths of the interstellar lines, are given. The agreement is very striking, being within 0.04 Å. Even for one line the probability that it coincides by mere chance with the $R(0)$ line of a band consisting of widely spaced lines is exceedingly small. The actual agreement for all three observed bands for which an agreement is to be expected proves beyond any doubt that the interstellar lines are due to the same molecule as the new laboratory bands, that is, that they are due to the CH+ molecule. The very small remaining difference is of the same order (0.04 Å) and in the same direction as found by McKellar (14) for CH. The difference is certainly outside the limit of accuracy of the laboratory measurements and, as pointed out by McKellar (14) and Adams (1), may possibly be due to a difference in radial velocity between interstellar Ca+ (which is used for calibration) and interstellar CH and CH+. While they considered a difference in the two systems of wave-lengths as also possible, the new results about CH+ seem to make the explanation by a difference in radial velocity more likely, particularly since the line 3957.72 lies between the two Ca+ lines (H and K).

TABLE VI

COMPARISON OF LABORATORY AND INTERSTELLAR WAVE-LENGTHS OF CH+ LINES

Band	λ(Å) of $R(0)$ of CH+ in the laboratory	Interstellar lines	Difference
0–0	4232.539	4232.58	−0.041
1–0	3957.700*	3957.72	−0.020
2–0	3745.310	3745.330	−0.020

* *The R(0) line of the 1–0 band is overlapped in the laboratory by the R(5) line. Therefore the measured wave-length does not exactly correspond to R(0). The value given here is not this directly measured wave-length but the value obtained from the band constants resulting from the other lines of the 1–0 band. It is considered to be just as reliable as the wave-lengths of the other lines.*

It was at first thought that the interstellar line 3579.04 is the $R(0)$ line of the 3–0 band of CH+. However, apart from the failure to observe this band in the laboratory there are two fairly strong reasons against this identification. (i) If the line 3579.04 is the $R(0)$ line of the 3–0 band it would be necessary to introduce a cubic term $\omega_e y_e(v + \frac{1}{2})^3$ with positive $\omega_e y_e$ into the formula for the vibrational levels (since $\Delta G'_{2\frac{1}{2}}$ would be 1242.2 cm.$^{-1}$ instead of the value 1226.44 cm.$^{-1}$ extrapolated from the ω_e' and $\omega_e x_e'$ values given in Table V). However, a positive value for $\omega_e y_e$ appears very unlikely in view of the negative value of γ_e' in Formula (2), since it is quite generally observed that the B_v and $\Delta G_{v+\frac{1}{2}}$ curves of a given electronic state have the same shape. (ii) If the value of $\omega_e' y_e'$ obtained from the identification in question is used to extrapolate the vibrational quanta of the upper state, it is found that for no value of v' do the vibrational quanta become equal to zero.

While these arguments are not entirely cogent it would appear unlikely that the line 3579.04 is due to CH^+. Probably it is due to some other ionized molecule whose laboratory spectrum is not yet known.

It is interesting to record that Swings (21)* on the basis of our data has identified CH^+ also in the spectra of comets. In addition he has discussed in greater detail the ionization and dissociation equilibrium of CH in interstellar space.

Acknowledgments

We are greatly indebted to the American Philosophical Society for a grant from the Penrose Fund through which the grating spectrograph was provided, and to the National Research Council of Canada for a grant that made possible our collaboration.

References

1. ADAMS, W. S. Astrophys. J. 93(1) : 11-23. 1941.
2. BACHER, R. F. and GOUDSMIT, S. Atomic energy states. McGraw-Hill Book Company, Inc., New York and London. 1932.
3. BEALS, C. S. and BLANCHET, G. H. Monthly Notices Roy. Astron. Soc. 98 : 398-407. 1938.
4. DOUGLAS, A. E. and HERZBERG, G. Astrophys. J. 94 : 381. 1941.
5. DUNHAM, T., JR. Pub. Astron. Soc. Pacific, 49 : 26. 1937.
6. DUNHAM, T., JR. and ADAMS, W. S. Pub. Astron. Soc. Pacific, 49 : 5. 1937.
7. GERÖ, L. and SCHMID, R. F. Phys. Rev. (Ser. 2) 60 : 363. 1941.
8. GERÖ, L. and SCHMID, R. F. Naturwissenschaften, 29 : 504. 1941.
9. HERZBERG, G. Molecular spectra and molecular structure. I. Diatomic molecules. Prentice-Hall, Inc., New York. 1939.
10. HERZBERG, G. and MUNDIE, L. G. J. Chem. Phys. 8(3) : 263-273. 1940.
11. KUSCH, P., HUSTRULID, A., and TATE, J. T. Phys. Rev. (Ser. 2) 52(8) : 843-854. 1937.
12. LEDOUX, P. Popular Astron. 49 : 513-523. 1941.
13. McDONALD, F. C. Abstract. Phys. Rev. (Ser. 2) 29(1): 212. 1927.
14. McKELLAR, A. Pub. Astron. Soc. Pacific, 52 : 187-192. 1940.
15. McKELLAR, A. Pub. Astron. Soc. Pacific, 52 : 312-318. 1940.
16. McKELLAR, A. Dominion Astrophys. Obs., Victoria, Pub. 7(15). 1942.
17. MERRILL, P. W. Pub. Astron. Soc. Pacific, 46 : 206. 1934.
18. MERRILL, P. W. and WILSON, O. C. Astrophys. J. 87(1) : 9-23. 1938.
19. MULLIKEN, R. S. and CHRISTY, A. Phys. Rev. (Ser. 2) 38(1) : 87-119. 1931.
20. SMITH, L. G. Phys. Rev. (Ser. 2) 51(4) : 263-275. 1937.
21. SWINGS, P. Astrophys. J. 95 : 270-280. 1942.
22. SWINGS, P. and ROSENFELD, L. Astrophys. J. 86(4) : 483-486. 1937.
23. THUNBERG, S. F. Z. Physik, 100 : 471-477. 1936.

---

* *We wish to thank Dr. Swings for letting us see a copy of the manuscript of his paper in advance of its publication.*

THE THEORY OF SOME A-C. COMMUTATOR MOTORS WITH SERIES CHARACTERISTICS

II. THE WINTER-EICHBERG COMPENSATED REPULSION MOTOR[1]

By E. G. Cullwick[2]

Abstract

The method of analysis applied to the simple repulsion motor, in Part I of this paper (1), is now used in a study of the characteristics of the Winter–Eichberg compensated repulsion motor. Elementary explanations of this machine often contain statements that the power factor becomes leading at high speeds, but this is not necessarily true. The effect of the circulating currents in the armature coils short-circuited by the brushes may well be such that the power factor is always lagging and never reaches unity. In the development of the current locus, it is shown how this interesting effect depends on the resistance of the short-circuited coils.

1. General Theory

In the compensated repulsion motor, Fig. 1, the rotor power current I_2 is induced by transformer action, as in the simple repulsion motor, in the *aa'* circuit. The *aa'* axis, however, is made coincident with the stator axis, and the speed field ϕ_b is produced by the current I_b through a second pair of brushes *bb'* at right angles to *aa'*. The "field" current I_b may be merely the stator current I_1, but a certain flexibility is obtained if the field circuit *bb'* is energized from the stator circuit through a transformer of variable ratio *a*. With connections as shown in Fig. 1, the direction of rotation will be clockwise.

Let the positive directions of currents and fluxes be as shown. Let ϕ_a and ϕ_b be the components of the total flux linking the rotor. For the power-

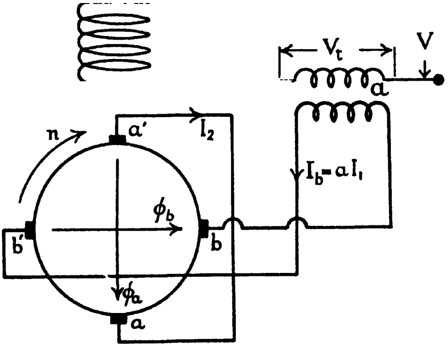


Fig. 1. *Compensated repulsion motor.*

---

[1] *Manuscript received in original form October 28, 1941, and as revised, February 9, 1942.*
Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Alta.

[2] *Professor and Head of Department.*

axis $a'a$, ϕ_a is the transformer field and ϕ_b the speed field. For the field axis bb', however, ϕ_a is the speed field and ϕ_b the transformer field. For the $a'a$ axis, therefore, the positive direction of the speed field (ϕ_b) lags behind the positive direction of the transformer field (ϕ_a), so that Equation (2)†* applies. Hence

$$\boldsymbol{E}_{aa'} = Q_2(-n\phi_b + jn_s\phi_a) = -\frac{n}{n_s}\boldsymbol{I}_b X_b + j(\boldsymbol{I}_1 X_{12} - \boldsymbol{I}_2 X_a), \tag{1}$$

where X_a is the rotor reactance between aa', and X_b is the reactance between bb'. Putting $\boldsymbol{I}_b = a\boldsymbol{I}_1$ and equating $\boldsymbol{E}_{aa'}$ to the resistance drop $\boldsymbol{I}_2 R_a$ in the aa' circuit gives

$$\boldsymbol{I}_2 = \frac{\boldsymbol{I}_1}{Z_a^2}\left\{ X_{12}(X_a + jR_a) - \frac{an}{n_s} X_b(R_a - jX_a) \right\}. \tag{2}$$

Considerable simplification will ensue if it may be assumed that $X_a \doteqdot X_b = X_2$ and $R_a \doteqdot R_b = R_2$. For the $b'b$ axis the positive direction of the speed field (ϕ_a) is in advance of the positive direction of the transformer field (ϕ_b), so that Equation (1)† applies. Hence:

$$\boldsymbol{E}_{bb'} = Q_2(n\phi_a + jn_s\phi_b) = \frac{n}{n_s}(\boldsymbol{I}_1 X_{12} - \boldsymbol{I}_2 X_2) + j\boldsymbol{I}_b X_2 . \tag{3}$$

The p.d. across the brushes is

$$\boldsymbol{V}_{b'b} = \boldsymbol{E}_{bb'} + \boldsymbol{I}_b R_2 , \tag{4}$$

and the p.d. across the primary of the transformer is $\boldsymbol{V}_t = a\boldsymbol{V}_{b'b}$, which from Equations (2), (3), and (4) becomes

$$\begin{aligned} \boldsymbol{V}_t = \boldsymbol{I}_1 \Bigg\{ & \left[a^2 R_2 + a\frac{n}{n_s}\left\{ X_{12} - \left(\frac{X_2}{Z_2}\right)^2 X_{12} \right\} + a^2\left(\frac{n}{n_s}\right)^2\left(\frac{X_2}{Z_2}\right)^2 R_2 \right] \\ & + j\left[a^2 X_2 - a\frac{n}{n_s}\frac{X_2 X_{12}}{Z_2^2} R_2 - a^2\left(\frac{n}{n_s}\right)^2\left(\frac{X_2}{Z_2}\right)^2 X_2 \right] \Bigg\}. \end{aligned} \tag{5}$$

Further, the p.d. across the stator winding is

$$\begin{aligned} \boldsymbol{V}_s & = \boldsymbol{I}_1(R_1 + jX_1) - j\boldsymbol{I}_2 X_{12} \\ & = \boldsymbol{I}_1 \Bigg\{ \left[R_1 + \left(\frac{X_{12}}{Z_2}\right)^2 R_2 + a\frac{n}{n_s}\left(\frac{X_2}{Z_2}\right)^2 X_{12} \right] \\ & \qquad + j\left[X_1 - \left(\frac{X_{12}}{Z_2}\right)^2 X_2 + a\frac{n}{n_s}\frac{X_{12}X_2}{Z_2^2} R_2 \right] \Bigg\} . \end{aligned} \tag{6}$$

The motor terminal p.d. is then $\boldsymbol{V} = \boldsymbol{V}_t + \boldsymbol{V}_s = \boldsymbol{I}_1 \boldsymbol{Z}_{st}$, where

$$\begin{aligned} \boldsymbol{Z}_{st} = & \left\{ R_1 + a^2 R_2 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 \right\} + j\left\{ X_1 + a^2 X_2 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 \right\} \\ & + a\frac{n}{n_s}\left\{ X_{12} + a\frac{n}{n_s} R_2\left(\frac{X_2}{Z_2}\right)^2 - ja\frac{n}{n_s} X_2\left(\frac{X_2}{Z_2}\right)^2 \right\}. \end{aligned} \tag{7}$$

The term a^2X_2 is the reactance of the "field winding" bb', and at synchronous speed is roughly compensated by the last term in Equation (7), which gives the rotational e.m.f. per ampere induced between *bb′* by the "transformer flux" ϕ_a ; hence the name "compensated" repulsion motor.* The vector diagram is shown in Fig. 2.

---

* *In this paper, a dagger (†) following an equation number indicates that the equation is the one bearing that number in Part I of this series (1).*

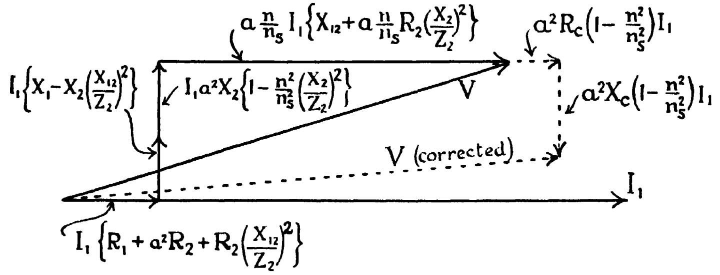

$a\frac{n}{n_S} I_1\left\{X_{12}+a\frac{n}{n_S}R_2\left(\frac{X_2}{Z_2}\right)^2\right\}$
$a^2R_c\left(1-\frac{n^2}{n_S^2}\right)I_1$
$I_1\left\{X_1-X_2\left(\frac{X_{12}}{Z_2}\right)^2\right\}$
$I_1a^2X_2\left\{1-\frac{n^2}{n_S^2}\left(\frac{X_2}{Z_2}\right)^2\right\}$
V
$a^2X_c\left(1-\frac{n^2}{n_S^2}\right)I_1$
V (corrected)
I_1
$I_1\left\{R_1+a^2R_2+R_2\left(\frac{X_{12}}{Z_2}\right)^2\right\}$

FIG. 2. *Compensated repulsion motor. Vector diagram. Dotted lines show the effect of the short-circuited coils.*

From Equation (7) it is found that the power factor is unity when

$$\left(\frac{n}{n_s}\right)^2 = \frac{X_1 + a^2X_2 - X_2(X_{12}/Z_2)^2}{a^2X_2(X_2/Z_2)^2} \,. \tag{8}$$

The copper loss is $P_c = I_1^2R_1 + (a^2I_1^2 + I_2^2)R_2$, whence, from Equation (2),

$$\frac{P_c}{I_1^2} = R_1 + a^2R_2 + R_2\left\{\left(\frac{X_{12}}{Z_2}\right)^2 + a^2\frac{n^2}{n_s^2}\left(\frac{X_2}{Z_2}\right)^2\right\} . \tag{9}$$

The gross motor power is equal to the input less the copper loss, or

$$P_m = I_1^2a\frac{n}{n_s}X_{12} \,. \tag{10}$$

The gross torque

$$T = 0.117\frac{P_m}{n}, \tag{10a}$$

---

* *If* $\mathbf{Z}_a \neq \mathbf{Z}_b$, *Equations (5), (6), (7) become:*

$$\boldsymbol{V_t/I_1} = \left\{a^2R_b + a\frac{n}{n_s}X_{12}\left(1 - \frac{X_a^2}{Z_a^2}\right) + a^2\left(\frac{n}{n_s}\right)^2\frac{X_aX_b}{Z_a^2}R_a\right\}$$
$$+ j\left\{a^2X_b - a\frac{n}{n_s}\frac{X_aX_{12}}{Z_a^2}R_a - a^2\left(\frac{n}{n_s}\right)^2\frac{X_a^2}{Z_a^2}X_b\right\} , \tag{5a}$$

$$\boldsymbol{V_s/I_1} = \left\{R_1 + \left(\frac{X_{12}}{Z_a}\right)^2R_a + a\frac{n}{n_s}\frac{X_aX_b}{Z_a^2}X_{12}\right\}$$
$$+ j\left\{X_1 - \left(\frac{X_{12}}{Z_a}\right)^2X_a + a\frac{n}{n_s}\frac{X_{12}X_b}{Z_a^2}R_a\right\} , \tag{6a}$$

and

$$\mathbf{Z}_{st} = \left\{R_1 + a^2R_b + R_a\left(\frac{X_{12}}{Z_a}\right)^2\right\} + j\left\{X_1 + a^2X_b - X_a\left(\frac{X_{12}}{Z_a}\right)^2\right\}$$
$$+ a\frac{n}{n_s}\left[\left\{X_{12} - \frac{X_aX_{12}}{Z_a^2}(X_a - X_b) + a\frac{n}{n_s}\frac{X_aX_b}{Z_a^2}R_a\right\}\right.$$
$$\left. - j\left\{\frac{R_aX_{12}}{Z_a^2}(X_a - X_b) + a\frac{n}{n_s}\left(\frac{X_a}{Z_a}\right)^2X_b\right\}\right] . \tag{7a}$$

If Equation (7a) is made the basis of the construction of the current locus in Fig. 3, the chief difference will be that the line RS will deviate slightly to the left of the vertical.

which is seen to be a function of the current only, as in other series motors. In terms of V and n

$$T = 0.117 \frac{aV^2}{n_s Z_a^2}\,, \tag{11}$$

which is a very complicated expression unless resistances are neglected. If this is done we have the approximation:

$$Z_a^2 \doteqdot \left(a\frac{n}{n_s}X_{12}\right)^2 + \left(X_1 + a^2X_2 - X_{12}^2/X_2 - a^2\frac{n^2}{n_s^2}X_2\right)^2, \tag{12}$$

so that

$$T \doteqdot 0.117\frac{V^2}{n_s}\frac{aX_{12}}{\left(a\frac{n}{n_s}X_{12}\right)^2 + \left(X_1 + a^2X_2 - X_{12}^2/X_2 - a^2\frac{n^2}{n_s^2}X_2\right)^2}. \tag{13}$$

The starting torque

Putting $n = 0$ in Equation (13) we have, neglecting resistances,

$$T_S \doteqdot 0.117\frac{V^2}{n_s}\frac{aX_{12}}{[X_1 + X_2\{a^2 - (X_{12}/X_2)^2\}]^2}. \tag{14}$$

Differentiating Equation (14) with respect to a, we find for the maximum starting torque for a given terminal p.d.:

$$a^2 = \frac{X_1X_2 - X_{12}^2}{3X_2^2}\,. \tag{15}$$

Example: If $X_1 = 51.5$, $X_2 = 6.57$, $X_{12} = 17.4$, the maximum starting torque with full-voltage starting is when $a = 0.525$.

2. Rough Approximations

If we neglect both resistance and leakage reactance, and assume that the winding coefficients are identical, we may put as before: $X_1 = cN_1^2$, $X_2 = cN_2^2$, $X_{12} = cN_1N_2$, whence

$$Z_{et} \doteqdot a\frac{n}{n_s}X_{12} + ja^2X_2(1 - n^2/n_s^2)\,. \tag{16}$$

Thus, in the "ideal" motor, the power factor is unity at synchronous speed, and this relation is independent of the transformer ratio a.

The power factor angle θ is given approximately by

$$\tan\theta \doteqdot a\frac{N_2}{N_1}\left(\frac{n_s^2 - n^2}{n_s n}\right), \tag{17}$$

so that the power factor can be improved at speeds above and below synchronism by reducing the ratio a by tap-changing on the transformer.

The power factor, neglecting resistance, but allowing for leakage. Let $N_1/N_2 = b$, and $x_e = x_1 + b^2x_2$ the equivalent leakage reactance of the motor, x_1 being the sum of the leakage reactances of stator and transformer referred to the primary. Then, from Equation (6*a*)†: $X_1X_2 - X_{12}^2 = X_{12}\frac{x_e}{b}$. Neglecting resistance we have from Equation (7):

$$\tan\theta = \frac{X_1X_2 - X_{12}^2 + a^2X_2^2(1 - n^2/n_s^2)}{a\frac{n}{n_s}X_2X_{12}}$$

$$= \frac{n_s}{n}\cdot\frac{x_e}{abX_2} + a\frac{X_2}{X_{12}}\left(\frac{n_s^2 - n^2}{n_s n}\right), \tag{18}$$

so that at synchronous speed:

$$\tan\theta \doteq \frac{x_e}{abX_2}. \tag{19}$$

3. Commutation in the Compensated Repulsion Motor

Referring to Fig. 1, we shall take the positive direction of the e.m.f's induced in the coils short-circuited by *aa'* as that which would cause a current having an m.m.f. from *b* to *b'*: i.e., opposed to the positive direction of ϕ_b. Similarly, we shall take the positive direction of the e.m.f's induced in the coils short-circuited by *bb'* as that which would cause a current having an m.m.f. opposed to the direction of ϕ_a.

Commutation at aa'. For the coil short-circuited by *aa'*, ϕ_b is the transformer field and ϕ_a the speed field. Since ϕ_a is in advance of ϕ_b it follows that Equation (1)† applies. Hence the e.m.f. induced in the shorted coil is

$$E_a = Q_s(n\phi_a + jn_s\phi_b).$$

From Equation (1):

$$\phi_a = \frac{I_1X_{12} - I_2X_2}{Q_2n_s}.$$

If resistances are neglected, this becomes, from Equation (2):

$$\phi_a = -jI_1\frac{X_2an}{Q_2n_s^2}, \tag{20}$$

and

$$\phi_b = a\frac{I_1X_2}{Q_2n_s}. \tag{21}$$

Let

$$\frac{Q_s}{Q_2}X_2 = X_{rm} \doteq \tfrac{1}{2}\pi\frac{N_s}{N_2}X_2, \tag{22}$$

the mutual reactance between the shorted coil and the rest of the rotor winding. Then

$$E_a = jaI_1X_{rm}\{1 - (n/n_s)^2\}, \tag{23}$$

and we see that the commutation at *aa'* is inherently good only at synchronous speed.

To find E_a at starting, neglecting resistance and leakage we have

$$aI_1 = \frac{aV}{Z_{st}} \doteq \frac{V}{jaX_2},$$

from Equation (16), so that

$$E_{a_{(n=0)}} \doteq \frac{X_{sm}}{X_2}\frac{V}{a}. \tag{24}$$

Thus the commutation at *aa′* can be improved at starting by increasing *a*. This, however, is at the expense of the starting torque (Equation (15)).

Commutation at bb′. For the coil short-circuited by *bb′*, ϕ_a is the transformer field and ϕ_b is the speed field. Since ϕ_b lags behind ϕ_a, Equation (2)† applies. Hence the e.m.f. induced in the shorted coil is

$$E_b = Q_s(-n\phi_b + jn_s\phi_a);$$

from Equations (20) and (21) this becomes

$$E_b \doteqdot aI_1X_{rm}\left(\frac{n}{n_s} - \frac{n}{n_s}\right) = 0 \tag{25}$$

Thus the inherent commutation at the excitation brushes *bb′* is good at all speeds, the only appreciable e.m.f. in the short-circuited coils being the usual "reactance voltage" caused by the current reversal.

4. The Effect of the Short-circuited Coils on the Performance of the Compensated Repulsion Motor

From Equation (25) it is seen that the effect of the currents in the coils short-circuited by *bb′* will be negligible. We shall confine our attention to the coils shorted by the power brushes *aa′*.

The short-circuit current in these coils is

$$I_s = \frac{E_a}{R_s + jX_s} = jaI_1\frac{X_{rm}}{Z_s^2}(R_s - jX_s)\{1 - (n/n_s)^2\} \tag{26}$$

in a direction opposed magnetically to ϕ_b. This current induces a transformer e.m.f. from *b* to *b′* given by

$$E_{bs} = -jI_sX_{sm} = aI_1\left(\frac{X_{rm}}{Z_s}\right)^2(R_s - jX_s)\{1 - (n/n_s)^2\}, \tag{27}$$

and a rotational e.m.f. between *a* and *a′* which is zero at both standstill and synchronism,* and which as in the case of the simple repulsion motor will be neglected. The terminal p.d. of the motor must therefore be increased by an amount equal to aE_{bs}, so that the equivalent impedance of the motor is increased by

$$Z' = a^2\frac{X_{rm}^2}{Z_s}(R_s - jX_s)\{1 - (n/n_s)^2\}, \tag{28}$$

which should be compared with Equations (33)† and (34)† for the simple repulsion motor. Putting

$$\left(\frac{X_{rm}}{Z_s}\right)^2 R_s = R_c, \quad \text{and} \quad \left(\frac{X_{rm}}{Z_s}\right)^2 X_s = X_c \tag{29}$$

we have

$$Z' = a^2(R_c - jX_c)\{1 - (n/n_s)^2\}. \tag{30}$$

The effect on the vector diagram is shown by the dotted lines in Fig. 2

---

* *See note at end of Part I of this series (1).*

The *copper loss* in the short-circuited coil is, as in the case of the simple repulsion motor (Equation (35)†),

$$I_s^2R_s = \frac{E_a^2}{Z_s^2}R_s = I_1^2a^2R_c\left(1 - \frac{n^2}{n_s^2}\right)^2 \tag{31}$$

and since the input is increased by $I_1^2a^2R_c\left(1 - \frac{n^2}{n_s^2}\right)$, the *gross power* is increased by

$$P_{mc} = I_1^2a^2R_c\frac{n^2}{n_s^2}\left(1 - \frac{n^2}{n_s^2}\right) \tag{32}$$

while the *gross torque* is increased by

$$T_c = 0.117\frac{P_{mc}}{n} \tag{33}$$

exactly as in the case of the simple repulsion motor.

We then have:

The equivalent standstill resistance

$$R'_e = R_1 + a^2R_2 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 + a^2R_c\,. \tag{34}$$

The equivalent standstill reactance

$$X'_e = X_1 + a^2X_2 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 - a^2X_c\,. \tag{35}$$

The rotational e.m.f.

$$E'_r = -I_1a\frac{n}{n_s}\left[X_{12} - a\frac{n}{n_s}\left\{R_2\left(\frac{X_2}{Z_2}\right)^2 - R_c - j\left[X_2\left(\frac{X_2}{Z_2}\right)^2 - X_c\right]\right\}\right]. \tag{36}$$

The copper loss is given by

$$\frac{P'_c}{I_1^2} = \frac{P_c}{I_1^2} + a^2R_c\left(1 - \frac{n^2}{n_s^2}\right)^2, \text{ where } P_c/I_1^2 \text{ is given by Equation (9).} \tag{37}$$

The gross motor power

$$P'_m = I_1^2a\frac{n}{n_s}\left\{X_{12} + aR_c\frac{n}{n_s}\left(1 - \frac{n^2}{n_s^2}\right)\right\}. \tag{38}$$

The gross torque

$$T' = 0.117\frac{P'_m}{n}. \tag{38a}$$

The total equivalent impedance

$$\begin{aligned} Z'_{et} = {} & \left\{R_1 + a^2R_2 + R_2\left(\frac{X_{12}}{Z_2}\right)^2 + a^2R_c\right\} + j\left\{X_1 + a^2X_2 - X_2\left(\frac{X_{12}}{Z_2}\right)^2 - a^2X_c\right\} \\ & + a\frac{n}{n_s}\left\{X_{12} + a\frac{n}{n_s}\left[R_2\left(\frac{X_2}{Z_2}\right)^2 - R_c\right] - ja\frac{n}{n_s}\left[X_2\left(\frac{X_2}{Z_2}\right)^2 - X_c\right]\right\}, \end{aligned} \tag{39}$$

which can easily be rearranged in the form $Z'_{et} = R'_{et} + jX'_{et}$.

5. The Current Locus for Constant Reactances

(*a*) *No correction for short-circuit currents*

In Fig. (3):

$$OX = X_1 + a^2X_2 - X_2\left(\frac{X_{12}}{Z_2}\right)^2$$

$$XR = R_1 + a^2R_2 + R_2\left(\frac{X_{12}}{Z_2}\right)^2$$

$$RS = \frac{n}{n_s}X_{12}, \qquad SN = \left(a\frac{nX_2}{n_sZ_2}\right)^2, \quad \tan y = \frac{R_2}{X_2}.$$

Then ON is the reflected impedance vector when short-circuit currents are neglected, and the locus of N is clearly a parabola, the inverse of which, with respect to O, is the current locus. The limits of *power factor* are:

Standstill $\tan\theta_s = OX/XR$, lagging,

Infinite speed $\tan\theta_\infty = X_2/R_2$, leading.

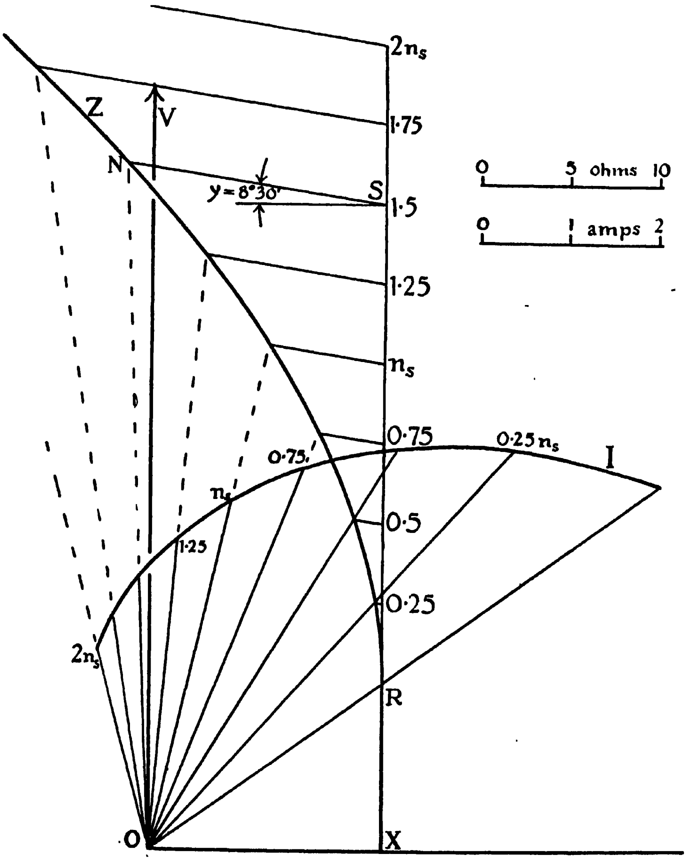


FIG. 3. *Compensated repulsion motor. Case (a), no correction.*

(*b*) ***Including the effect of the short-circuited coils***

This is shown in Fig. 4, in which:

$$OX' = OX - a^2X_c, \quad X'R' = XR + a^2R_c, \quad R'S' = a\frac{n}{n_s}X_{12},$$

$$S'N' = a^2\frac{n^2}{n_s^2}\sqrt{R_r^2 + X_r^2}, \text{ where } R_r = R_2\left(\frac{X_2}{Z_2}\right)^2 - R_c$$

$$\text{and } X_r = X_2\left(\frac{X_2}{Z_2}\right)^2 - X_c.$$

$$\tan y' = R_r/X_r.$$

The locus of the impedance vector is then $R'N'$, which crosses the locus RN of Fig. 3 at synchronous speed.

The sign of X_r depends on the value of R_s. If both R_2 and R_s are zero, we have in the "ideal motor", from Equations (29) and (22) and Equation (31)†:

$$X_c \doteqdot \frac{X_{rm}^2}{X_s} \doteqdot \frac{\pi}{2}X_2, \qquad \text{and} \qquad X_r = -\left(\frac{\pi}{2} - 1\right)X_2,$$

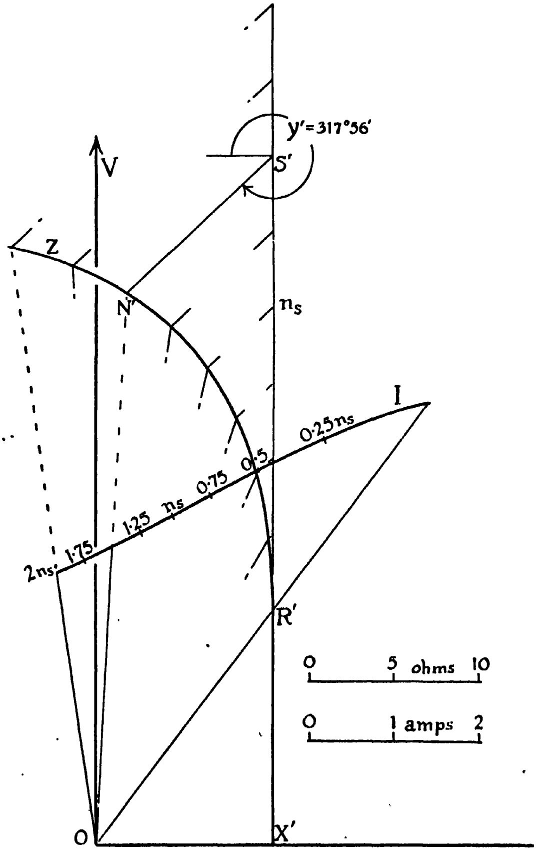


FIG. 4. *Compensated repulsion motor. Case (b), R_s = 0.5.*

in which case the locus $R'N'$ curves to the right and the power factor never becomes unity.

There are three possible cases according to the relative magnitudes of $X_2(X_2/Z_2)^2$ and X_c:

(*A*) $X_c < X_2(X_2/Z_2)^2$. The impedance locus $R'N'$ is a parabola curving to the left as in Fig. 4, and the power factor passes through unity and becomes leading at high speeds.

(*B*) $X_c = X_2(X_2/Z_2)^2$. The impedance locus is a vertical straight line as shown in Fig. 5, and the current locus is a circle. Further, if $R_c < R_2(X_2/Z_2)^2$, the power factor reaches unity at infinite speed, but if $R_c > R_2(X_2/Z_2)^2$ the power factor increases until $n = \frac{X_{12}}{2aR_r} n_s$, and then decreases.

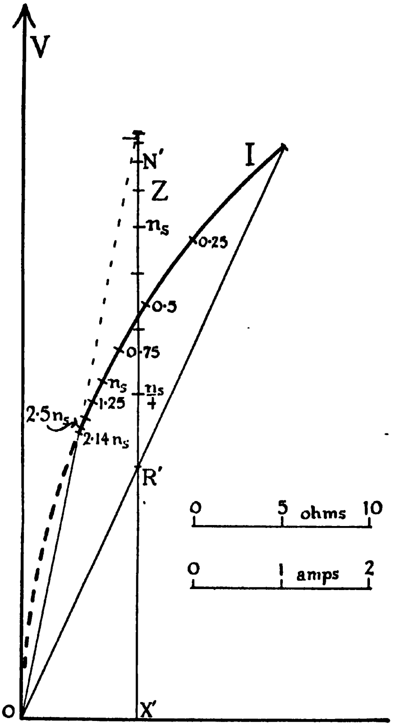


FIG. 5. *Compensated repulsion motor. Case (c),* $R_s = 0.224$. *Maximum P.F. = 0.980 at 2.14* n_s. *Minimum current = 3.28 amp.*

(*C*) $X_c > X_2(X_2/Z_2)^2$. The impedance locus is a parabola curving to the right, as shown in Fig. 6., and the power factor rises to a maximum value (lagging) at some finite speed and never becomes leading.

Example. As an example, suppose the previous figures* refer to a compensated repulsion motor, for which $a = 1$. Then: $X_2 = 6.57, X_2(X_2/Z_2)^2 = 6.42, X_s = 0.286, X_{rm} = \frac{6.57\pi}{6 \times 2} = 1.719, R_2 = 0.98$. Table I gives the data for the construction of the current locus for each of the two cases: (*a*) No

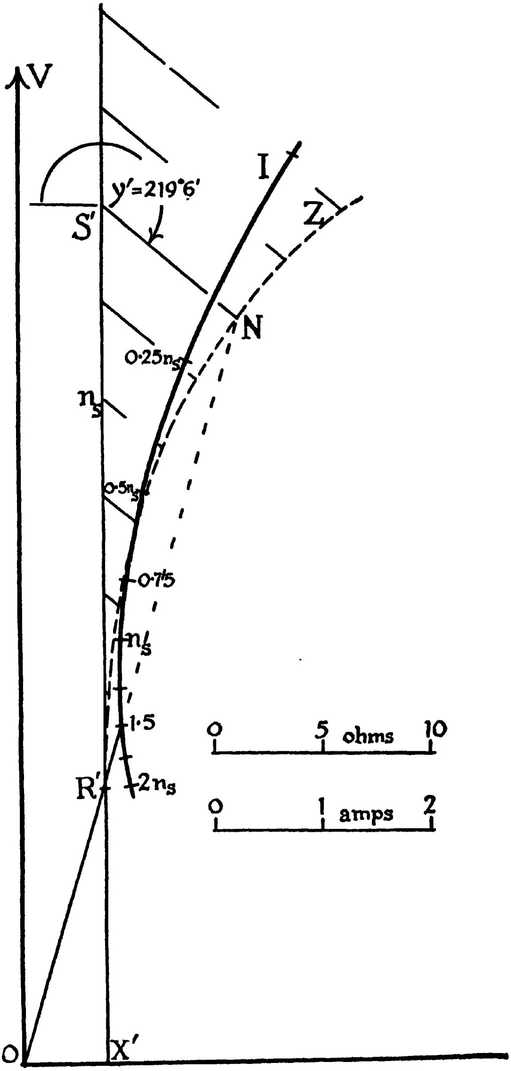


FIG. 6. *Compensated repulsion motor. Case (d),* $R_s = 0.1$. *Maximum P.F.* $= 0.976$ *at* $n = 0.55\ n_s$.

---

* *Part I of this series (1).*

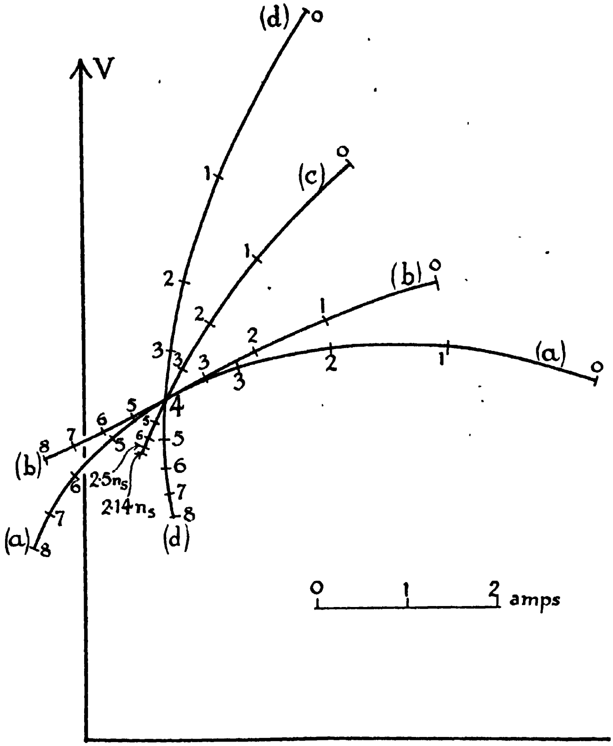


FIG. 7. *Compensated repulsion motor. Current loci. (a) No correction, (b) $R_s = 0.5$, (c) $R_s = 0.224$, (d) $R_s = 0.1$. Figures denote quarters of synchronous speed.*

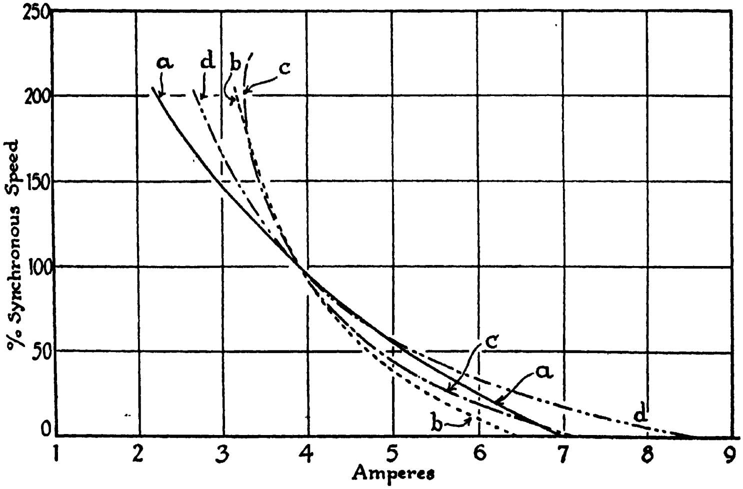


FIG. 8. *Compensated repulsion motor. Effect of short-circuited coils on speed-current curves.*

correction for short-circuit currents, Fig. 3; (*b*) $R_s = 0.5$, Fig. 4; (*c*) $R_s = 0.224$, Fig. 5; and (*d*) $R_s = 0.1$, Fig. 6.

TABLE I

DATA FOR FIGS. 3, 4, 5, AND 6

	OX	XR	RS			SN	y
(*a*) No correction Fig. 3	13.0	9.08	$17.4\frac{n}{n_s}$			$6.5\left(\frac{n}{n_s}\right)^2$	8°30′
	OX'	$X'R'$	$R'S'$	R_r	X_r	$S'N'$	y'
(*b*) $R_s = 0.5$ Fig. 4	10.45	13.53	$17.4\frac{n}{n_s}$	−3.49	3.87	$5.21\left(\frac{n}{n_s}\right)^2$	317°56′
(*c*) $R_s = 0.224$ Fig. 5*	6.58	14.10	$17.4\frac{n}{n_s}$	−4.06	0	$4.06\left(\frac{n}{n_s}\right)^2$	270°
(*d*) $R_s = 0.1$ Fig. 6	3.8	12.3	$17.4\frac{n}{n_s}$	−2.26	−2.78	$3.58\left(\frac{n}{n_s}\right)^2$	219°6′

* *That is,* $R'N' = 17.4\frac{n}{n_s} - 4.06\left(\frac{n}{n_s}\right)^2$, *and is vertical.*

The current loci for the four cases are shown superimposed in Fig. 7 in which it is seen that they all intersect at synchronous speed. The figures 1, 2, 3, . . . shown along the loci denote quarters of synchronous speed. Current-speed curves for the four cases are shown in Fig. 8.

In these diagrams the speed has been extended above the theoretical no-load speed, at which the gross torque (Equation (38*a*)) becomes zero. It differs slightly in the three cases, but is in the neighbourhood of $1.75\ n_s$.

6. The Effect of Saturation

If resistances and leakage reactance are neglected, it is found that

$$\phi_b = KaI_1N_2\,,\quad \text{and}\quad \phi_a = -jKaI_1N_2\frac{n}{n_s} = -j\phi_a\frac{n}{n_s}\,,$$

so that at synchronous speed the windings produce a "rotating" m.m.f. of constant amplitude proportional to aI_1N_2. Hence the values of the reactances, neglecting the variation due to departure from synchronous speed, should be found as follows:

(1) Given curves showing X_1 and X_{12} as functions of I_1, the values of X_{12} and X_1 for a given stator current I_1 under operating conditions are those corresponding to a current equal to $aI_1N_2/N_1 \doteqdot aX_{12}I_1/X_1$ on the X_1 and X_{12} graphs.

(2) The value of X_2 is that corresponding to a current $I_b = aI_1$ on the X_2/I_b curve.

References

1. CULLWICK, E. G. Can. J. Research, A, 20 : 49-70. 1942.
2. FORD, W. Elec. Rev. 103 : 595-598. 1928.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. A. JULY, 1942 NUMBER 7

THE THEORY OF SOME A-C. COMMUTATOR MOTORS WITH SERIES CHARACTERISTICS

III. THE THREE-PHASE SERIES MOTOR[1]

By E. G. Cullwick[2]

Abstract

The method previously used in a study of repulsion motors is now applied to the case of the three-phase series motor. This machine, although little used as yet on this continent, has many points of interest. It runs at a high power factor, and its operating characteristics are readily modified by shifting the brushes. As before, the effect of the coils short-circuited by the brushes is studied. Experimental and theoretical results are then compared, and in computing the theoretical performance the effects of short-circuited coils and of saturation are taken into account.

1. Introduction

This motor, invented by Görges in 1891, is shown in its simplest form in Fig. 1. The brush axis of any one phase (such as AO) is displaced through an angle β from the axis aa' of the stator winding. Each phase is therefore equivalent to a simple single-phase series motor, and the direction of the motor torque and of the rotation will be in the direction of brush-shift from the position of exact opposition of stator and rotor; that is, counter-clockwise in the case of Fig. 1.

The motor is therefore equivalent to three single-phase motors superimposed in such a way that the stator axes are displaced by 120° in time-phase. Owing to this symmetrical three-phase arrangement, however, the operating characteristics differ from those of the single-phase motor in certain ways: (1) The motor torque is constant instead of pulsating; (2) The space-fundamental components of the phase fluxes combine to form a constant "rotating field", rotating at synchronous speed in a direction fixed by the phase-sequence of the supply.

The induced e.m.f's in stator and rotor may be calculated most readily by means of this "rotating field" simile, although of course such e.m.f's are due fundamentally to both rotational and transformer action.

Provided that the direction of rotation of the motor is the same as that of the rotating field, no e.m.f. will be induced in the rotor at synchronism. The inherent commutation should therefore be good at speeds near synchronism,

---

[1] *Manuscript received in original form October 28, 1941, and as revised, February 9, 1942.*

Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Alta.

[2] *Professor and Head of Department.*

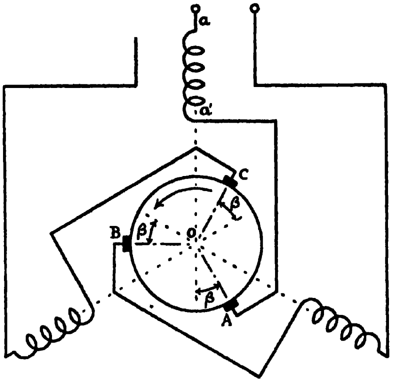


FIG. 1. *Three-phase series motor.*

but care must be taken to ensure the same direction for rotor and rotating field: the direction of rotation of the rotor depends on the direction of brush-shift and not on the phase sequence, and if the phase sequence is reversed the motor will still operate, but with very poor commutation and power factor.

If a rotor with commutator is driven at speed n and three-phase brushes are supplied with three-phase current at a frequency giving a synchronous speed n_s, the phase-sequence and direction of n being the same, the reactive e.m.f. induced in the rotor winding for a given current will be proportional to $n_s - n$. That is, the rotor acts as a three-phase load of balanced reactance proportional to $n_s - n$, so that at speeds below synchronism the reactance is positive (inductive) while at speeds above synchronism the reactance is negative (capacitive). This is the principle of operation of Scherbius phase-advancers, so that the power factor of the motor may be expected to improve as the speed increases, and at some speed above synchronism it should become leading.

If, however, the phase-sequence is reversed, the rotor will have a positive reactance proportional to $n + n_s$, which will continually increase as the speed increases, giving a poor power factor and bad commutation owing to the high e.m.f. induced in the coils short-circuited by the brushes.

In practice, in order to obtain good commutation over a wide range of speed, it is found desirable to make the number of rotor turns considerably smaller than the number of stator turns. To obtain approximate equality of stator and rotor m.m.f's a three-phase transformer is placed between stator and rotor as in Fig. 2.

In the following theory the presence of the transformer will be ignored, since if all measurements are made on the primary side the results will give effective values referred to the primary, and hence applicable in all equations relating to the primary circuit. For the high currents taken at low speeds, however, saturation of the transformer may complicate matters owing to the increase in magnetizing current.

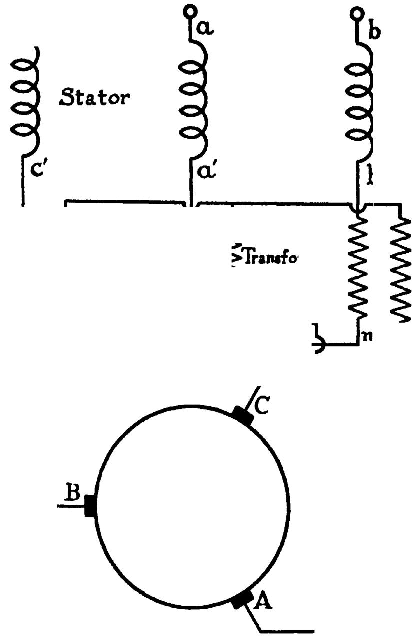


FIG. 2. *Three-phase series motor with inter-winding transformer.*

2. Theory Neglecting the Effect of Short-circuited Coils

Consider the e.m.f.'s induced in phase a. Let A represent the resultant rotating m.m.f. due to all three phases, its components being A_1 and A_2 due to the stator and rotor currents respectively. The rotating m.m.f. A_1 will be directed along the stator axis of phase a when the current in that phase is a maximum, and at the same instant A_2 will be directed along the brush axis AO (Fig. 1). The relations between A, A_1, and A_2 at this instant are shown in Fig. 3. As before, the flux ϕ and its components ϕ_1 and ϕ_2 may be taken as being approximately in-phase with the m.m.f's.

The total stator flux, $\phi_1 + \phi_{L_1}$, will induce an e.m.f. in the stator:

$$E_{s1} = -jIX_1 . \tag{1}$$

The rotor-component of mutual flux, ϕ_2, will induce an e.m.f. in the stator which will lag behind E_{s1} by the phase angle $\pi - \beta$, so that

$$E_{s2} = -jIX_{12}e^{-j(\pi-\beta)} = -IX_{12}(\sin\beta - j\cos\beta). \tag{2}$$

The total stator e.m.f. is therefore

$$E_s = E_{s1} + E_{s2} = -I[X_{12}\sin\beta + j(X_1 - X_{12}\cos\beta)]. \tag{3}$$

The flux component ϕ_1 will have its maximum linkage with the rotor phase at an angle $\pi + \beta$ later than the instant of its maximum linkage with the

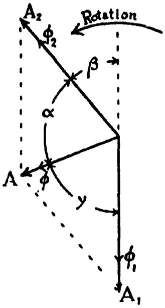


FIG. 3. *Components of magnetomotive force.*

stator. Thus, since its speed is $n_s - n$ relative to the rotor, it induces a rotor e.m.f. per phase:

$$E_{r1} = -jQ_2(n_s - n)\phi_1 e^{-j(\pi+\beta)} = IX_{12}\left(1 - \frac{n}{n_s}\right)(\sin\beta + j\cos\beta). \quad (4)$$

The total rotor-component of flux, $\phi_2 + \phi_{L2}$, will induce an e.m.f. in the rotor which will be in-phase with E_{s1}, so that

$$E_{r2} = -jIX_2\left(1 - \frac{n}{n_s}\right). \quad (5)$$

(This is the "reactance e.m.f." of the rotor of a Scherbius phase-advancer.) The total rotor e.m.f. is then

$$E_r = E_{r1} + E_{r2} = I\left(1 - \frac{n}{n_s}\right)[X_{12}\sin\beta - j(X_2 - X_{12}\cos\beta)]. \quad (6)$$

The terminal p.d. per phase is

$$V = -E_s - E_r + IR, \quad (7)$$

where R is the effective resistance per phase of the motor and is given by

$$R = R_1 + r_1 + a_t^2(R_2 + r_2), \quad (8)$$

where R_1 = resistance of stator phase; R_2 = resistance of rotor phase; r_1 = resistance of transformer primary, per phase; r_2 = resistance of transformer secondary, per phase, and a_t = transformer ratio.

The p.d. across a stator phase is $V_s = -E_s + IR_1$, or

$$V_s = I[R_1 + X_{12}\sin\beta + j(X_1 - X_{12}\cos\beta)]. \quad (9)$$

The p.d. across the transformer primary is

$$\begin{aligned} V_t &= -E_r + (R - R_1)I \\ &= I\left[R - R_1 - \left(1 - \frac{n}{n_s}\right)X_{12}\sin\beta + j(X_2 - X_{12}\cos\beta)\right], \end{aligned} \quad (10)$$

and the terminal p.d. is $V = IZ_{st}$, where

$$\begin{aligned} Z_{st} = &\left(R + \frac{n}{n_s}X_{12}\sin\beta\right) \\ &+ j\left\{(X_1 + X_2 - 2X_{12}\cos\beta) - \frac{n}{n_s}(X_2 - X_{12}\cos\beta)\right\}. \end{aligned} \quad (11)$$

The second half of the j-term is the cause of the high or leading power factor at high speeds.

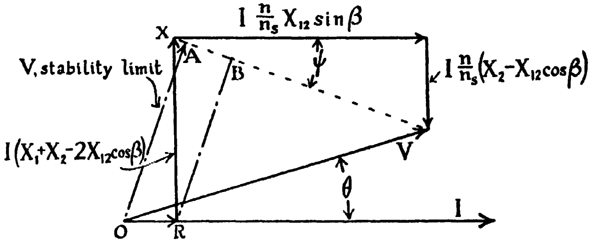

$I \frac{n}{n_s} X_{12} \sin\beta$
X
A
B
ψ
V, stability limit
$I \frac{n}{n_s}(X_2 - X_{12}\cos\beta)$
$I(X_1+X_2-2X_{12}\cos\beta)$
V
θ
I
O
R

FIG. 4. *Vector diagram, three-phase series motor.*

The vector diagram per phase is shown in Fig. 4, from which it is seen that the angle ψ is given by

$$\tan\psi = \frac{X_2 - X_{12}\cos\beta}{X_{12}\sin\beta}. \qquad (12)$$

The gross motor power is

$$P_m = I^2 \frac{n}{n_s} X_{12}\sin\beta. \qquad (13)$$

The gross torque is

$$T = 0.117 \frac{P_m}{n} \text{ lb. ft.} \qquad (14)$$

The minimum stable speed

It is seen from the vector diagram that the equivalent impedance, Z_{et}, is not necessarily a minimum at standstill. The minimum value, and hence the maximum value of the gross torque, will occur at a finite speed n_0 such that the vector V is perpendicular to the vector XA (Fig. 4). This condition, which gives maximum current for a given p.d., gives the minimum speed, n_0, at which the motor will operate stably. We have, in Fig. 4:

$$XA = XB - AB = XR\sin\psi - OR\cos\psi,$$

whence

$$XA^2 = \frac{n_0}{n_s}\{(X_1 + X_2 - 2X_{12}\cos\beta)(X_2 - X_{12}\cos\beta) - RX_{12}\sin\beta\},$$

which gives for the speed n_0:

$$\frac{n_0}{n_s} = \frac{(X_2 - X_{12}\cos\beta)(X_1 + X_2 - 2X_{12}\cos\beta) - RX_{12}\sin\beta}{X_{12}^2\sin^2\beta + (X_2 - X_{12}\cos\beta)^2}, \qquad (15)$$

which shows that under certain conditions, for a particular brush angle, the maximum torque can occur at starting. If resistance is neglected, this condition is given by $X_2 = X_{12}\cos\beta$.

The determination of n_0 can, of course, be performed graphically instead of by the use of Equation (15).

As a further approximation, let us neglect leakage and assume the stator and rotor winding factors to be equal. We may then put $X_1 = cN_1^2$, $X_2 =$

cN_2^2, $X_{12} = cN_1N_2$, whence Equation (15) reduces to

$$\frac{n_0}{n_s} \div 1 - \frac{N_1}{N_2}\cos\beta\ , \tag{16}$$

a result given by Rüdenberg for an "ideal" motor (5, p. 233).

Effect of transformer ratio

If N_2 in Equation (16) is the actual number of rotor turns, and the transformer ratio is a_t, then the speed n_0 is, for the same approximations, given by

$$\frac{n_0}{n_s} \div 1 - \frac{N_1}{a_tN_2}\cos\beta\,. \tag{17}$$

The value of the maximum torque, neglecting resistances

Putting $n/n_s = n_0/n_s$ in Equation (11), we find for the value of Z_{st} at the minimum stable speed, when resistance is neglected:

$$(Z_{st0})^2 \div \frac{(X_{12}\sin\beta)^2(X_1 + X_2 - 2X_{12}\cos\beta)^2}{X_{12}^2\sin^2\beta + (X_2 - X_{12}\cos\beta)^2}\ , \tag{18}$$

whence, putting $I^2 = (V/Z_{st})^2$ in Equation (14), we find

$$T_{max} \div \frac{0.117\ V^2}{n_s}\ \frac{(X_2^2 - 2X_2X_{12}\cos\beta + X_{12}^2)}{X_{12}\sin\beta\ (X_1 + X_2 - 2X_{12}\cos\beta)^2}\,. \tag{19}$$

The starting torque

Neglecting resistances; we have $(Z_{st})_{n=0} = X_1 + X_2 - 2X_{12}\cos\beta$, so that

$$T_S \div \frac{0.117\ V^2}{n_s}\ \frac{X_{12}\sin\beta}{(X_1 + X_2 - 2X_{12}\cos\beta)^2}\,. \tag{20}$$

The ratio

$$\frac{\text{Maximum torque}}{\text{Starting torque}} \div 1 + \left(\frac{X_2 - X_{12}\cos\beta}{X_{12}\sin\beta}\right)^2\,. \tag{21}$$

Thus the maximum torque can occur at standstill only if $X_2 \div X_{12}\cos\beta$.

3. The Effect of the Currents in the Short-circuited Coils

The positive direction of the e.m.f's induced in the coil short-circuited by the brush A is shown by the dotted and crossed conductors in Fig. 5. It is such that it will cause a current having a m.m.f. in the direction m_s. The e.m.f. induced in the short-circuited coil is found as follows.

The flux-component ϕ_1 will have its maximum linkage with the shorted coil at an instant $\pi/2 + \beta$ later than with the stator phase. The e.m.f. in the coil due to ϕ_1 is therefore

$$\begin{aligned} e_{c_1} &= -jQ_s(n_s - n)\phi_1 e^{-j(\frac{\pi}{2}+\beta)} \\ &= -IX_{sm_1}\left(1 - \frac{n}{n_s}\right)(\cos\beta - j\sin\beta), \end{aligned} \tag{22}$$

where X_{sm1} is equal to the flux-linkages per ampere with the shorted coil due to the stator flux ϕ_1 of all three phases.

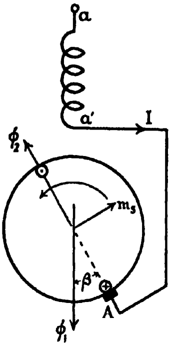


FIG. 5. *Direction of e.m.f's in a coil short-circuited by a brush.*

The flux ϕ_2 will have its maximum linkage at an angle $\alpha + y = \pi - \beta$ later than the flux ϕ_1; that is, $\pi/2 + \beta + \pi - \beta = 3\pi/2$ later than the instant of maximum linkage of ϕ_1 with the stator phase. It will therefore induce an e.m.f. in the coil:

$$e_{c_2} = -jQ_s(n_s - n)\phi_2 e^{-j3\pi/2} = IX_{sm_2}\left(1 - \frac{n}{n_s}\right). \tag{23}$$

For simplicity, assume $X_{sm1} \doteqdot X_{sm2} = X_{sm}$; then the total e.m.f. in the shorted coil is

$$e_c = IX_{sm}\left(1 - \frac{n}{n_s}\right)(1 - \cos\beta + j\sin\beta). \tag{24}$$

The current in the shorted coil, due to e_c, is $I_c = e_c/(R_s + jX_s)$, where X_s, the reactance of the shorted coils of one phase considered as one coil, must include the mutual reactances with the shorted coils of the other two phases. Then

$$I_c = \frac{IX_{sm}(1 - n/n_s)}{Z_s^2}$$
$$[\{R_s(1 - \cos\beta) + X_s\sin\beta\} + j\{R_s\sin\beta - X_s(1 - \cos\beta)\}]. \tag{25}$$

This current combines with similar currents in the coils shorted by the brushes of the other two phases to set up a field rotating at speed n_s relative to the stator. This field has its maximum linkage (in the positive direction) with the stator phase a at an angle $3\pi/2 - \beta$ later than the instant of maximum current. The e.m.f. induced in the stator is therefore

$$E_{sc} = -jI_cX_{sm}e^{-j(3\pi/2-\beta)} = jI_cX_{sm}(\sin\beta - j\cos\beta). \tag{26}$$

Substituting for I_c from Equation (25) we get

$$E_{sc} = -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)$$
$$[R_s(1 - \cos\beta) - X_s\sin\beta - j\{R_s\sin\beta + X_s(1 - \cos\beta)\}]. \tag{27}$$

The rotating field of the short-circuit currents will have its maximum linkage with the rotor phase $\pi - \beta$ *earlier* than with the stator phase; that is, $\pi/2$

later than the instant of maximum current. The transformer e.m.f. induced in the rotor is then:

$$E_{rc} = -jI_cX_{sm}e^{-j\pi/2} = -I_cX_{sm} = -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1-\frac{n}{n_s}\right)$$
$$[R_s(1-\cos\beta)+X_s\sin\beta+j\{R_s\sin\beta-X_s(1-\cos\beta)\}]. \quad (28)$$

As in the case of the repulsion motor, the corresponding rotational e.m.f. in the rotor is neglected. The total e.m.f. induced per phase by the short-circuit currents is therefore

$$E_c = E_{sc}+E_{rc} = -2I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1-\frac{n}{n_s}\right)(1-\cos\beta)(R_s-jX_s). \quad (29)$$

The terminal p.d. is increased by $-E_c$. The equivalent *total* impedance of the motor is increased by

$$Z' = (1-\cos\beta)\left(1-\frac{n}{n_s}\right)(R_c-jX_c), \quad (30)$$

where

$$R_c = 2R_s\left(\frac{X_{sm}}{Z_s}\right)^2 \quad \text{and} \quad X_c = 2X_s\left(\frac{X_{sm}}{Z_s}\right)^2. \quad (31)$$

The input per phase is increased by

$$I^2R_c(1-\cos\beta)\left(1-\frac{n}{n_s}\right). \quad (32)$$

The copper loss in the shorted coil (per phase) is

$$I_c^2R_s = \frac{e_c^2}{Z_s^2}R_s = I^2R_c(1-\cos\beta)\left(1-\frac{n}{n_s}\right)^2. \quad (33)$$

The gross power is increased by

$$P_{mc} = I^2R_c(1-\cos\beta)\left(1-\frac{n}{n_s}\right)-I_c^2R_s$$
$$= I^2R_c\frac{n}{n_s}\left(1-\frac{n}{n_s}\right)(1-\cos\beta), \quad (34)$$

which is zero both at standstill and synchronism.

The gross torque, per phase, is increased by

$$T_c = 0.117\frac{P_{mc}}{n}. \quad (35)$$

The equivalent true resistance (giving the total copper losses), per phase, now becomes:

$$R_s' = R+R_c(1-\cos B)\left(1-\frac{n}{n_s}\right)^2. \quad (36)$$

The equivalent standstill reactance is

$$X_s' = X_1+X_2-2X_{12}\cos\beta-X_c(1-\cos\beta). \quad (37)$$

The component of p.d. which cancels the rotational e.m.f. now becomes

$$-E_r = I\frac{n}{n_s}[X_{12}\sin\beta-j(X_2-X_{12}\cos\beta)-(1-\cos\beta)(R_c-jX_c)]. \quad (38)$$

The total equivalent impedance is

$$\begin{aligned} Z'_{et} = {} & R + R_c(1 - \cos\beta) + \frac{n}{n_s}\{X_{12}\sin\beta - R_c(1 - \cos\beta)\} \\ & + j\Big[X_1 + X_2 - 2X_{12}\cos\beta - X_c(1 - \cos\beta) \\ & \qquad - \frac{n}{n_s}\{X_2 - X_{12}\cos\beta - X_c(1 - \cos\beta)\}\Big]. \end{aligned} \tag{39}$$

The gross motor power becomes

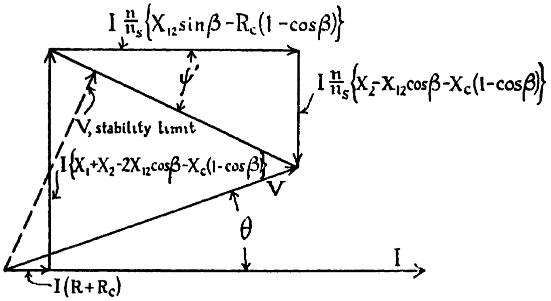
$$P_m' = P_m + P_{mc} = I^2\frac{n}{n_s}\left[X_{12}\sin\beta + R_c(1 - \cos\beta)\left(1 - \frac{n}{n_s}\right)\right]. \tag{40}$$

The starting torque. Neglecting resistances, this becomes

$$T_S' = \frac{0.117\ V^2}{n_s}\,\frac{X_{12}\sin\beta}{\{X_1 + X_2 - 2X_{12}\cos\beta - X_c(1 - \cos\beta)\}^2}. \tag{41}$$

The vector diagram

The vector diagram, when the effect of the shorted coils is included, is shown in Fig. 6, which should be compared with Fig. 4.



$I\frac{n}{n_s}\{X_{12}\sin\beta - R_c(1-\cos\beta)\}$
ψ'
$I\frac{n}{n_s}\{X_2 - X_{12}\cos\beta - X_c(1-\cos\beta)\}$
β
V, stability limit
$I\{X_1 + X_2 - 2X_{12}\cos\beta - X_c(1-\cos\beta)\}$
V
θ
I
$I(R+R_c)$

FIG. 6. *Vector diagram, three-phase series motor, allowing for the effect of the short-circuited coils.*

It is seen that the angle ψ' is given by

$$\tan\psi' = \frac{X_2 - X_{12}\cos\beta - X_c(1 - \cos\beta)}{X_{12}\sin\beta - R_c(1 - \cos\beta)}. \tag{42}$$

4. The Current Locus for Constant Reactances

The current loci, with and without the correction for the short-circuit currents, are circles that intersect at the origin and at the point corresponding to synchronous speed. The circles are shown in Fig. 7; the construction is as follows:

Uncorrected for effect of shorted coils	*Corrected for effect of shorted coils*
$OX = X_1 + X_2 - 2X_{12}\cos\beta$	$OX' = OX - X_c(1 - \cos\beta)$
$XR = R$	$X'R' = XR + R_c(1 - \cos\beta)$
$\tan\psi = \dfrac{X_2 - X_{12}\cos\beta}{X_{12}\sin\beta}$	$\tan\psi'$ given by Equation (42).
The uncorrected current locus is the inverse of the line RN with respect to the origin O. It is a circle, centre C, passing through the origin.	The corrected current locus is the inverse of the line $R'N'$ with respect to the origin O. It is a circle, centre C', passing through the origin.

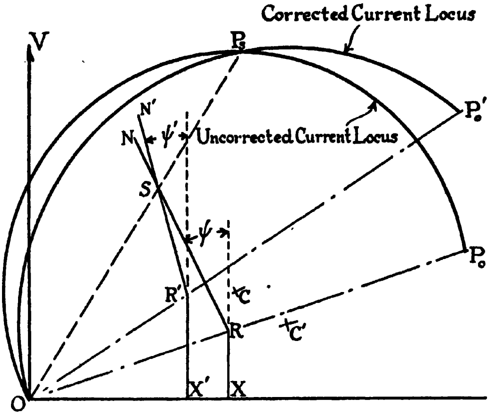


FIG. 7. *Three-phase series motor, circle diagrams.*

The two circles intersect at the point P_s, which represents synchronous speed. Further, the lines RN and $R'N'$ intersect at S, corresponding to the impedance vector at synchronous speed. RN and $R'N'$ can be calibrated as speed scales.

It is seen that at standstill (P_0 and P_0') the corrected circle gives a higher current, power, and power factor than the uncorrected case. Except at synchronous speed, for a given power input the effect of the shorted coils is to increase the current and reduce the power factor. The maximum possible power input is also reduced.

5. Measurement of the Reactances

(A) R_c and X_c

Let the rotor be open-circuited and ordinary impedance measurements made on the stator. Then the flux ϕ_1 induces an e.m.f. in the short-circuited coil equal to e_{c1} (Equation (22)). The flux ϕ_2 is absent so that the current induced in the coil is

$$I_c = \frac{e_{c1}}{R_s + jX_s}$$

$$= -I\frac{X_{sm}\left(1 - \frac{n}{n_s}\right)}{Z_s^2}[R_s\cos\beta + X_s\sin\beta + j(X_s\cos\beta - R_s\sin\beta)].$$

This current induces an e.m.f. in the stator

$$E_s = jI_cX_{sm}(\sin\beta - j\cos\beta),\ \text{as before,}$$

$$= -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)(R_s - jX_s), \qquad (43)$$

which is independent of β. That is, the position of the brushes in this test is immaterial.

Thus at *standstill*, the apparent reactance of the stator is *decreased by*

$$X_s\left(\frac{X_{sm}}{Z_s}\right)^2 = \tfrac{1}{2}X_c, \tag{44}$$

and the apparent resistance in *increased* by

$$R_s\left(\frac{X_{sm}}{Z_s}\right)^2 = \tfrac{1}{2}R_c. \tag{45}$$

(B) Stator reactance, X_1

With reference to Fig. 2, a', b', and c' are disconnected from the transformer and joined together in a star point. The brushes are lifted. Measurements are then made with a balanced variable three-phase supply at the stator terminals *a–b–c*, for a current varying from a low value up to about rated load current.

If I, V, W, and R are per-phase values, X_1 is given by Equation 49†*, or approximately by Equation 48†. If the test is repeated with the brushes down, X_c may be obtained from Equation (44).

The mutual reactance, X_{12}

This may be found in three ways.

(a) Stator to rotor. The stator winding is connected as for the measurement of X_1. The brushes are left down and, in addition to stator amperes, volts, and watts (I, V, W), the rotor phase volts, V_2, are measured across the open-circuited primary of the transformer *a′n*. $(X_{12} - \tfrac{1}{2}X_c)$ is given roughly by V_2/I, but to allow for the stator resistance and core loss angle we have, from the vector diagram shown in Fig. 8:

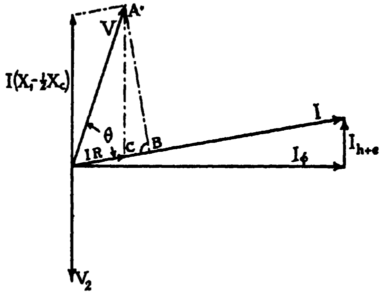


FIG. 8. *Vector diagram showing the effect of core loss.*

$$X_{12} - \tfrac{1}{2}X_c = \frac{V_2}{I_\phi} = \frac{V_2 I}{I\,I_\phi} = \frac{V_2\,.\,AC}{I\,.\,AB} = \frac{V_2\,I(X_1 - \tfrac{1}{2}X_c)}{I\,V\sin\theta}$$

$$= \frac{V_2}{I}\sqrt{\frac{V^2 + I^2R^2 - 2WR}{V^2 - W^2/I^2}} \tag{46}$$

From the same test we obtain $X_1 - \tfrac{1}{2}X_c$, and hence X_c.

---

* *In this paper, a dagger (†) following an equation number indicates that the equation is the one bearing that number in Part I of this series (2).*

(b) Rotor to stator. The connections are the same as in *(a)* except that three-phase power is supplied to the primary of the transformer, and the voltage V_2 in Equation (46) is that across the open-circuited stator, aa'.

The two values of X_{12} so obtained should be found to give a reasonable check. They can be plotted on a base of I and a mean value taken in calculations.

(c) From the equivalent leakage reactance, x_e. If x_e is determined by short-circuit tests, X_{12} may be found by means of Equation 6†. This is found in practice to be the most satisfactory method.

The rotor reactance (referred to stator), X_2

The readings V, I, W on the primary side of the transformer in test *(b)* for X_{12} will give:

$$X_2 + X_t - \tfrac{1}{2}X_c = \frac{\sqrt{V^2 + I^2R^2 - 2WR}}{I}, \tag{47}$$

where X_t is the equivalent leakage reactance of the transformer and is found in the usual manner. Whence, knowing X_c, X_2 is found and plotted on a base of I.

Determination of the reactances under running conditions

If at any particular speed we measure *(a)* supply volts, amperes, and watts, *(b)* p.d. across a stator phase, and *(c)* p.d. across the transformer primary, we may determine X_1, X_2, and X_{12} (neglecting the effect of the shorted coils). For from *(a)* we can calculate Z_{et}, and Equations (9), (10), and (11) are sufficient to find the three reactances and the resistance $R - R_1$, while R_1 can be measured directly. The equations reduce to their simplest form at synchronous speed.

The effective resistance, R

The resistance R is given by Equation (8), where R_1, r_1, and r_2 are constant but R_2 includes the variable brush-contact resistance. Hence for accurate results R must be taken, like the reactances, as a function of the current I.

From the results of the test for X_2 we may obtain an equivalent resistance $R_e = W/I^2$ which, in addition to $r_1 + a^2(R_2 + r_2)$, includes $\tfrac{1}{2}R_c$ and also a fictitious resistance r_c such that I^2r_c is equal to the core loss. The core loss, for a given current, is a maximum at standstill and is difficult to calculate at a given speed. Hence we shall be on the safe side if we include its effect in R_e thus obtained. The total effective resistance per phase is then given by

$$R = R_1 + R_e \tag{48}$$

which can be plotted as a function of I, and in which $\tfrac{1}{2}R_c$ appears as a rough approximation for $R_c(1 - \cos\beta)$.

6. The Effect of Saturation

In Fig. 3 put $A_2 = A_1/a$, where a is the equivalent turns ratio, stator to rotor, and is given by

$$a = \frac{N_1k_1}{a_tN_2k_2}; \tag{49}$$

then $A = yA_1$, where

$$y = \frac{\sqrt{1 - 2a\cos\beta + a^2}}{a}. \tag{50}$$

If $a = 1$, this reduces to

$$y = 2\sin\frac{\beta}{2}. \tag{51}$$

If the motor current is I, then the flux-density is produced by the m.m.f. $A = yA_1$. The measured values of X_1, X_2, and X_{12} are found, and plotted, as functions of I, under conditions in which the stator and rotor m.m.f's act separately. Since the resultant magnetizing current under running conditions is yI, the values of X_1, etc., for a motor current I are those that correspond to a current $I' = yI$ on the graphs of X on I.

7. Experimental Results for a Three-phase Series Motor

The motor was a 3-phase Oerlikon machine with inter-winding transformer, 4-pole, 60 cycles, 220 volts, 4.5–8 h.p., in the Electrical Engineering Laboratory of the University of British Columbia.

Winding data

Stator: 48 slots; 15 conductors in series per slot; star-connected; $k_1 = 0.957$; conductors in series per pole per phase $= Z_1 = 60$.

Rotor: 42 slots; 6 conductors in series per slot; delta connected; $k_2 = 0.957$.

Commutator: 126 segments; one turn per segment. One brush set per phase per pair of poles. Each brush shorts two turns most of the time. That is, two conductors in series per pole per phase are shorted by the brushes. The actual conductors in series per pole per phase = 21.

Effective conductors per pole per phase = 21 − 2 = 19. Effective conductors per pole per phase, equivalent star connection, $= Z_2 = 19/\sqrt{3} = 10.95$.

Transformer ratio: $a_t = 5.6$.

Transformer leakage reactance: $X_t = 0.07$.

Stator/rotor equivalent turns ratio:

$$a = \frac{Z_1 k_1}{a_t Z_2 k_2} = \frac{60}{5.6 \times 10.95} = 0.98 \doteqdot \text{unity}.$$

The reactances, etc., were determined as outlined in Sections 1–6. Fig. 9 shows values of : $(a)\,X_1$, $(b)\,X_1 - \frac{1}{2}X_e$, $(c)\,X_2 + X_t - \frac{1}{2}X_e$, $(d)\,X_{12} - \frac{1}{2}X_e$, all plotted on a base of resultant magnetizing current I'. Curve (d) is plotted from the mean of two tests, stator to rotor and rotor to stator. Fig. 10 shows values of X_e, the equivalent leakage reactance, and R, the effective resistance, which are functions of the actual current I.

The method of calculation of the speed and power factor for an arbitrary current is illustrated by the following example.

$\beta = 30°$. Current $I = 17.8$ amp. $y = 2 \sin \frac{1}{2}\beta = 0.518$. $I' = yI = 9.22$. $X_1 = 10.81$, $X_1 - \frac{1}{2}X_c = 8.72$; $X_2 + X_t - \frac{1}{2}X_c = 8.75$; $R = 1.25$, so that

$$X_c = 4.18,\ X_2 = 10.77.$$

$$X_e = 0.90,\ X_{12} = \sqrt{X_1 X_2} - \tfrac{1}{2}X_e = 10.34.$$

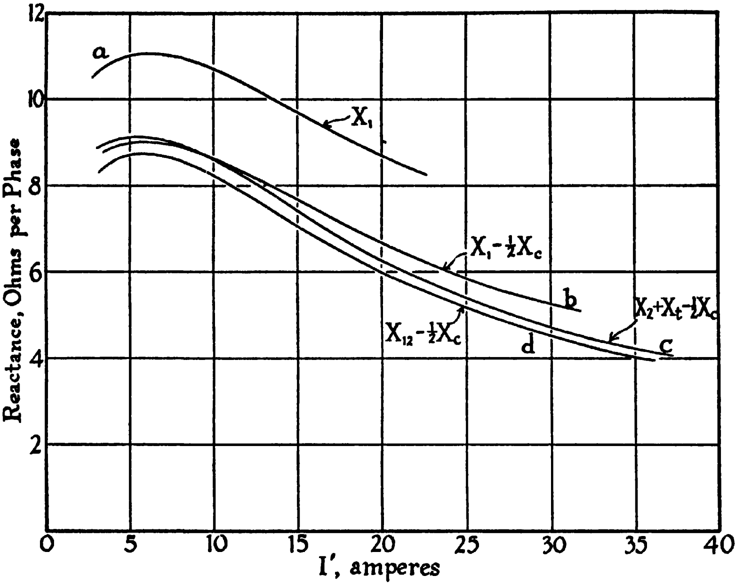


FIG. 9. *Reactance curves of three-phase series motor.*

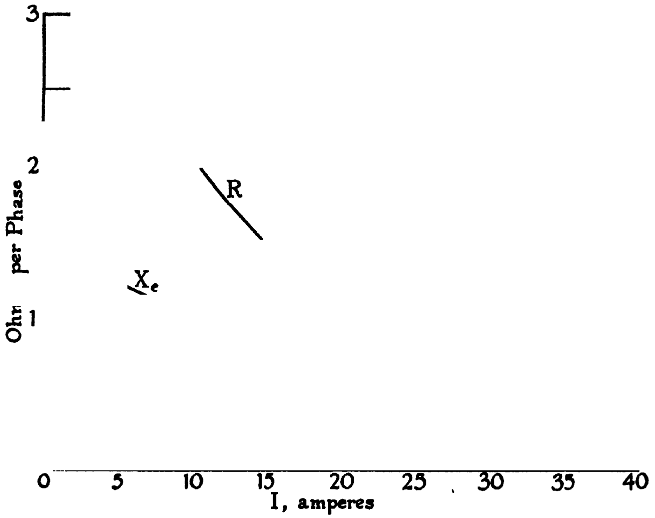


FIG. 10. *Three-phase series motor. Total effective resistance and leakage reactance.*

Whence, from Equation (39)

$$Z'_{st} = \left(1.25 + 5.17\frac{n}{n_s}\right) + j\left(3.180 - 1.255\frac{n}{n_s}\right) = \frac{220}{\sqrt{3} \times 17.8} = 7.135 \text{ ohms}$$

(scalar value), which gives the quadratic:

$$28.304\left(\frac{n}{n_s}\right)^2 + 4.943\frac{n}{n_s} - 39.233 = 0,$$

whence

$$\frac{n}{n_s} = 1.093, \quad \text{and} \quad n = 1.093 \times 1800 = 1967 \text{ r.p.m.}$$

(cf. 2090 r.p.m. measured)

The power factor

We have

$$R'_{st} = 1.25 + 1.093 \times 5.17 = 6.901,$$

$$\cos\theta = R'_{st}/Z'_{st} = 6.901/7.135 = 0.967 \text{ (cf. 0.968 measured).}$$

The calculated results are compared with experimental values for $\beta = 30°$, $40°$, and $50°$ in Figs. 11 and 12.

On the whole, the correspondence is good. The disturbing factors which have not been taken into account are: *(a)* the variation of R_e with *speed*, owing to variation of core loss. R_e was measured under conditions of high core loss (standstill) so that one would expect the error due to this cause to be greatest near synchronous speed, and to decrease as the speed deviates from synchronism. This tendency is shown in the curves of Figs. 11 and 12.

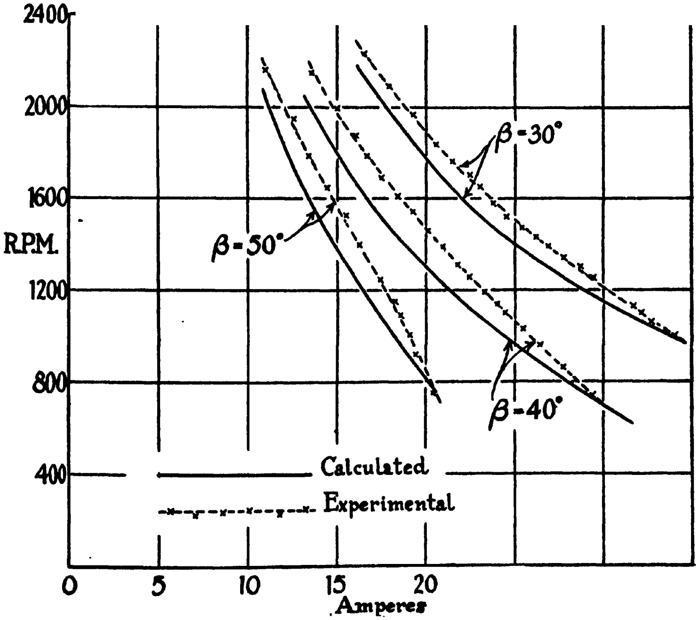


FIG. 11. *Results for three-phase series motor.*

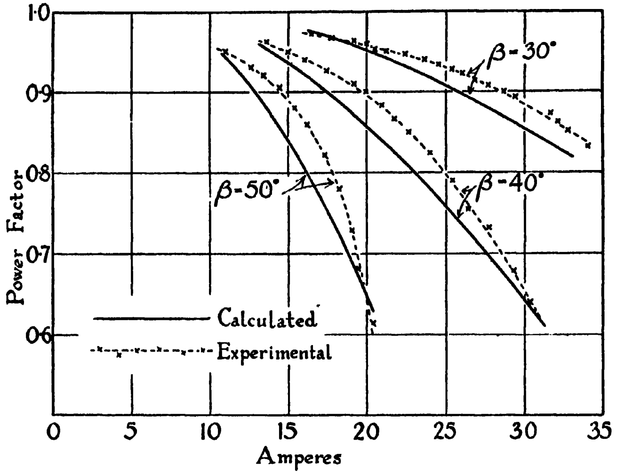


FIG. 12. *Results for three-phase series motor.*

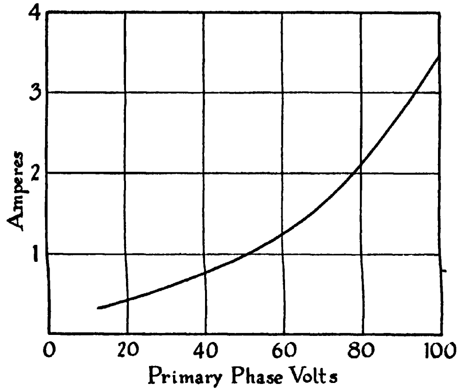


FIG. 13. *Three-phase series motor. Magnetizing current of inter-winding transformer.*

(b) The effect of the magnetizing current of the transformer: the magnetizing current flows through the stator of the motor but not through the rotor, and hence causes an error in the assumption that the equivalent current is the same in both windings. The magnetizing current is shown in Fig. 13 as a function of the p.d. across the transformer primary. This effect will be a minimum near synchronism, and is difficult to calculate since it will depend on the phase of the magnetizing current and this will vary with the speed. *(c)* For values of $\beta < 60°$, R_e is too large since it includes $\frac{1}{2}R_c$ as an approximation to $R_c\,(1 - \cos \beta)$. *(d)* When both windings carry current, the ratio of X_{12} to X_1 and X_2 will be slightly different from the values obtained when only one winding is energized, since both stator and rotor teeth will have normal saturation. *(e)* The rotational e.m.f. caused by the currents I_0 has been neglected.

Acknowledgments

The author wishes to express his indebtedness to Mr. W. J. Lind for his help at the University of British Columbia, in obtaining the experimental results for the three-phase motor given in Section 7; to Mr. D. C. Hutchinson for his assistance at the University of Alberta, in working out the theoretical results for the same machine; and to Dr. H. J. MacLeod, Head of the Department of Mechanical and Electrical Engineering at the University of British Columbia, for obtaining the leakage reactance of the inter-winding transformer and the information contained in Fig. 13.

References

1. BINDER, L. Elektrotech. Z. 34 : 410-414. 1913.
2. CULLWICK, E. G. Can. J. Research, A, 20(5) : 49-70. 1942.
3. KOSTENKO, M. and SAWALISCHIN, D. Elektrotech. u. Maschinenbau, 49 : 101-107. 1931.
4. ROBINSON, D. M. J. Inst. Elec. Engrs. (London) 69 : 1036-1040. 1931.
5. RÜDENBERG, R. Elektrotech. Z. 32 : 233-237. 1911. (See also, 31 : 1181-1183 and 1221-1224. 1910.)
6. SCHUISKY, W. Elektrotech. u. Maschinenbau, 49 : 333-339. 1931.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. AUGUST, 1942 NUMBER 8

LATERAL SUPPORT OF STEEL COLUMNS AND STRUTS[1]

BY C. R. YOUNG[2] AND W. B. DUNBAR[3]

Abstract

Experimental investigation of 19 full-size steel columns was undertaken to disclose *(a)* the merit of a lateral stay member that does not fix the direction of the column at the point of support, *(b)* the effectiveness of a stay member that connects to one edge only of the column width, *(c)* the effect on the required lateral support of initial column curvature or eccentricity, and *(d)* the maximum stress for which a stay member should be proportioned.

The results obtained appear to warrant the following conclusions:

(1) The percentage increase in the ultimate capacity of columns due to the introduction of lateral support is greatest for columns with high slenderness ratios and least for those with low slenderness ratios.

(2) For a column hinged at both ends, and having end eccentricity of loading up to one-eighth of the column width in the direction of bending, the introduction of lateral support at mid-height, without rotational fixing at this point, raises the strength to from 2.70 to 4.87 times the theoretical strength of the full-length column as computed by the secant formula.

(3) The necessary lateral supporting force of an eccentrically loaded, deflected column, where the lateral force is applied at the middle of the width of the section, is given with sufficient exactness by Equation (22),

$$Q_w = \frac{5P}{l}(\Delta \pm 1.33e) - \frac{48EIn}{l^3}.$$

(4) The relation between the necessary lateral supporting force applied at the edge of the section and that applied at the middle of the section width for a given deflection of the flange under consideration is given satisfactorily by Equation (23). For the test columns, which had widths of section normal to the plane of bending varying from 6 in. to 15⅜ in. and were subjected to loads up to 2.5 times the Euler load for a laterally unsupported column, the lateral supporting force when applied to the edge of a flange was in no case more than 15% greater than that which would have been necessary if applied to the middle of the web at the same flange deflection.

I. Introduction

1. Nature of the Problem

The capacity of a column or strut of a given cross section and length is admittedly greatly increased by preventing it from deflecting laterally at, or near, the point where this deflection would be greatest if no support were provided. The amount of the benefit has, however, been a matter of some uncertainty, as has the necessary capacity of the supporting or stay member serving to shorten the column.

Some of the questions that have been raised are:

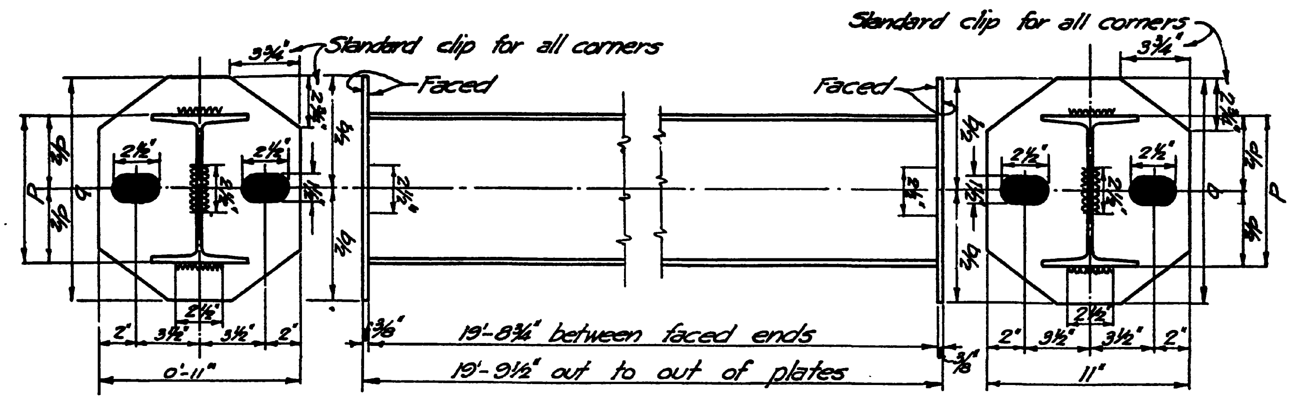
---

[1] *Manuscript received in original form August 1, 1941, and as revised, June 12, 1942.*

Contribution from the Faculty of Applied Science and Engineering, University of Toronto, Toronto, Ont., with financial assistance from the National Research Council of Canada.

[2] *Dean, Faculty of Applied Science and Engineering.*

[3] *Assistant Professor of Engineering Drawing.*


Standard clip for all corners
Faced
3¾"
2¾"
2½"
1½"
b/2
d/2
b
d
2"
3½"
0'-11"
⅜"
19'-8¾" between faced ends
19'-9½" out to out of plates
11"

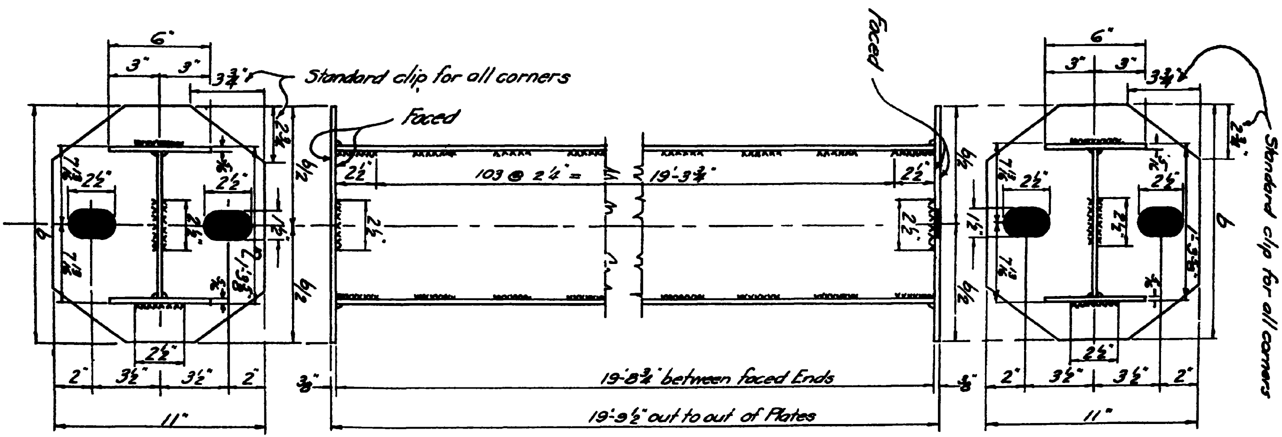
No. of specimens	Mark	Section	Plate	
			Stock	*b*
3	*C1A*, *C1B*, *C1C*. (alike)	6 in. - 17 25 # I	11 × ½ in.	9 in.
2	*C2A*, *C2B*. (alike)	7 in. - 20.0 # I	11 × ½ in.	10 in.
2	*C3A*, *C3B*. (alike)	10 in. - 16.5 # B.J.	11 × ½ in.	1 ft. - 1 in.
2	*C4A*, *C4B*. (alike)	9 in. - 25.0 # I	11 × ½ in.	1 ft. - 0 in.
2	*C5A*, *C5B*. (alike)	12 in. - 31.8 # I	11 × ½ in.	1 ft. - 3 in.
2	*C6A*, *C6B*. (alike)	9 in. - 20.5 # CM.	11 × ½ in.	1 ft. - 0 in.
2	*C7A*, *C7B*. (alike)	10 in. - 28.5 # B	11 × ½ in.	1 ft. - 1 in.
2	*C8A*, *C8B*. (alike)	12 in. - 28.0 # C	11 × ½ in.	1 ft. - 3 in.

Fillet welds ⅜ by ⅜ in.

NOTE

1. Column shaft must be perfectly straight.
2. Ends of columns to be faced absolutely parallel, not merely ground or chipped, before welding on plates.
3. Plates to be located centrically and have full contact over faced ends of column when welded.
4. Outside faces of plates to be faced absolutely parallel, not merely ground or chipped, after welding to faced column ends.
5. Plates may be ½ in. or $\frac{7}{16}$ in. thick, but must not be more than ½ in. thick after final facing.
6. Final length of column out to out of plates must be exact.
7. Initial length of column shaft to be about 6 in. longer than finally required. This 6 in. length to be cold sawn from shaft, marked same as column, and delivered to purchaser.

FIG. 1. *Schedule of rolled columns.*



No. required	Column		End plates			Mark
	Plates	Length	Stock	*b*	Slot	
2	2 — 6 in. × 5/16 in., 1 — 15 in. × 5/16 in.	19 ft. - 8¾ in.	11 × ½ in.	1 ft. - 6 in.	2½ × 1½	*C9A* and *C9B*

NOTE

1. **Column shaft must be perfectly straight after welding.**
2. **Ends of column to be faced *absolutely parallel*, not *merely* ground or chipped *before welding* on plates.**
3. **Plates to be located centrically and have full contact over faced ends of column, when welded.**
4. **Outside faces of end plates to be faced *absolutely parallel, not merely* ground or chipped, after welding to faced column ends.**
5. Plates may be ½ in. or 7/16 in. thick but must not be more than ⅜ in. thick after final facing.
6. Final length of column out to out of plates must be exact.
7. *Welding of flange plates to the web to be carried on in a way to prevent local warping between welds or general warping of whole column.*
8. ⅜ in. fillet welds.

FIG. 2. *Schedule of welded columns.*

(a) What is the merit of a stay member that does not fix the direction of the column at the point of support?

(b) How effective is a stay member that connects to one edge only of the column width, as, for example, a girt to a side column of a mill building?

(c) How is the value of a given lateral support affected by initial column curvature, or by eccentricity, either in the direction of the initial curvature, or in the opposite direction?

(d) For what axial load should a stay member be designed for the most critical of the above conditions?

The investigation here reported was directed to the answer of these and related questions.

II. Experimental Work

2. *Specimens*

All the test columns were made free to turn at the ends and were 20 ft. long between centres of end pivots. The testing equipment available restricted to 310,000 lb. the maximum axial load that could be applied. Within these limits the sections were so chosen, as is evident from Table I, as to give a progression in the maximum slenderness ratio of roughly 30, taking the length, *l*, for this purpose as the full length of the column, centre to centre of pivots.

TABLE I

PROPERTIES AND ULTIMATE LOADS OF THE TEST COLUMNS

All columns were 20 ft. long, centre to centre of pivots

Column mark	Section	Area, A, sq. in.	Minimum radius of gyration r, in.	Maximum slenderness ratio $\frac{l}{r}$ for $l = 240$ in.
C1A	6-in., 17.25-lb. I	5.02	0.68	353
C1B	6-in., 17.25-lb. I	5.02	0.68	353
C1C	6-in., 17.25-lb. I	5.02	0.68	353
C2A	7-in., 20-lb. I	5.83	0.74	324.3
C2B	7-in., 20-lb. I	5.83	0.74	324.3
C3A	10-in., 16.5-lb. B.J.	4.86	0.79	303.9
C3B	10-in., 16.5-lb. B.J.	4.86	0.79	303.9
C4A	9-in., 25-lb. I	7.28	0.88	272.9
C4B	9-in., 25-lb. I	7.28	0.88	272.9
C5A	12-in., 31.8-lb. I	9.26	1.01	237.7
C5B	12-in., 31.8-lb. I	9.26	1.01	237.7
C6A	9-in., 20.5-lb. C.M.	6.02	1.15	208.7
C6B	9-in., 20.5-lb. C.M.	6.02	1.15	208.7
C7A	10-in., 28.5-lb. B.	8.41	1.30	184.6
C7B	10-in., 28.5-lb. B.	8.41	1.30	184.6
C8A	12-in., 28-lb. C.	8.22	1.53	156.9
C8B	12-in., 28-lb. C.	8.22	1.53	156.9
C9A	1—15 × 5/16-in. pl. 2— 6 × 5/16-in. pls.	8.44	1.16	206.9
C9B	1—15 × 5/16-in. pl. 2— 6 × 5/16-in. pls.	8.44	1.16	206.9

Nineteen columns were fabricated and tested. Seventeen of these were simple rolled sections, ranging from a 6-in., 17.25-lb. I to a 12-in., 28-lb. C, as shown in Fig. 1. Two were sections built up of three plates into I-form by welding, as shown in Fig. 2. The depth of these sections, 15⅝ in., was made as great as could be accommodated in the machine, after making provision for the necessary auxiliary loading equipment.

3. Testing Equipment

As the available 400,000 lb. Riehlé testing machine could not, with the type of roller end bearings adopted for the test columns, accommodate columns more than 9.4 ft. long between end pivots, it was necessary, in order to load a specimen, to offset it 2 ft. 2 in. from the centre of the machine and to allow it to pass through the floor above. A test specimen, partly obscured by the near standard of the machine, is seen in position for test in Fig. 3.

The load was applied to the top of the column by means of two built-up loading eye-bars bolted to a loading cap. The necessary pull in these eye-bars was developed by pin-connecting them at the lower end to an end panel point of a loading truss, to the apex joint of which the testing machine applied through a spherical head any load up to the capacity of the machine. The far support of this truss is shown at the right in Fig. 3.

Lateral loads were applied to the test column by means of one or other of two gauge-equipped, 12-ton, horizontally placed hydraulic jacks. Each of these bore against a vertical lateral-loading beam, shown to the left in Fig. 3. Test columns were so oriented that the buckling would always take place in a plane parallel to the plane of the web of the lateral-loading beam, that is, either to the North (to the right in Fig. 3) or to the South.

In order that the buckling of the column in either sense might be met by a compressive, rather than a tensile, force, the test column, eye-bars, and lateral loading beam were girdled by a lateral loading frame carried on ball bearings moving on another support frame suspended as shown in the upper left-hand corner of Fig. 3 and in Fig. 4. If the test column tended to buckle to the North, its movement could be resisted by one jack forcing the frame with the attached loading screw, which bears against the column, to the South. If the column tended to buckle to the South, its movement could be countered directly by the other jack.

To reduce the uncertainty that frequently arises with respect to the degree of restraint existing at the ends of a column, and to be able to relate the actual to the theoretical performance, the test column was loaded at each end through roller bearings, especially manufactured for this research. These showed an average coefficient of friction under actual operating conditions of only about 0.0002.

The hydraulic jacks were provided with gauges originally intended for reading the lateral loads. It was found, however, that the friction on the ram was such a large factor in the comparatively small lateral loads that

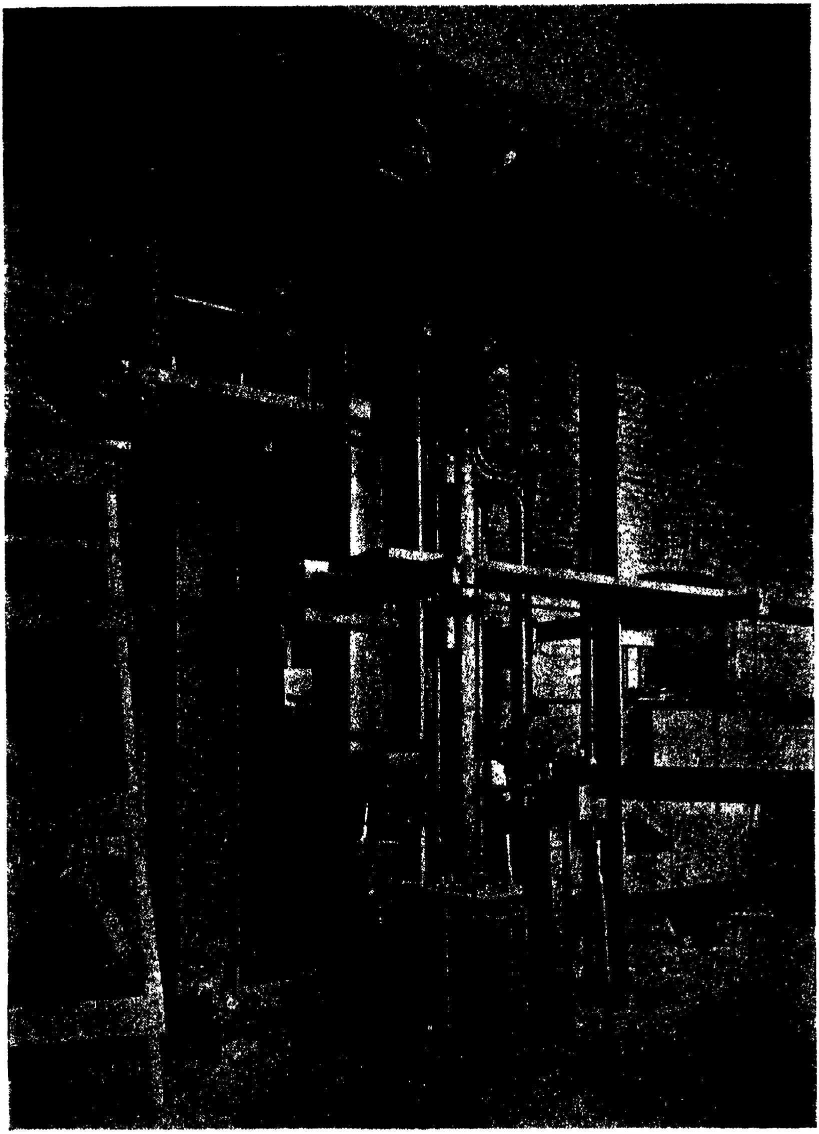


FIG. 3. *General view of testing apparatus from the Southeast.*

reliance could not be placed on the gauges. Friction also prevented the flexibility that was desirable in applying the loads.

For this reason, spring dynamometers of 1000 lb., and later 3000 lb., capacity (3) were developed. These were used on the head of the jacks and were read in place of the gauges on the jacks.

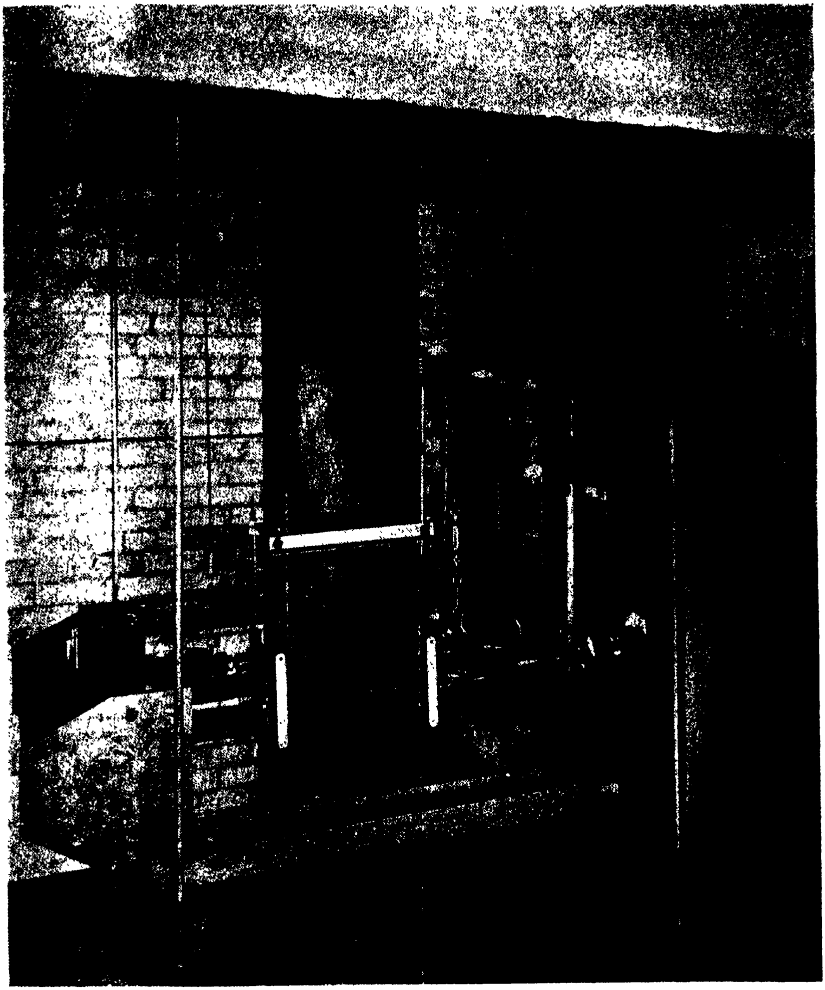


FIG. 4. *Jacks and dynamometer in position for web support, portion of lateral loading frame being removed.*

In order that the test column might not be subjected to a large initial dead load, a counterbalancing steelyard device was introduced between an overload trolley and the lifting eye in the loading cap, whereby the column was relieved of the dead load tension in the loading eye-bars, the weight of the loading cap and the upper roller bearing. The only initial load on the column was, therefore, its own weight.

4. Testing Procedure

General. One of the objectives of the investigation being the determination of the necessary lateral supporting force at mid-height with a given deflection and a given axial load, it was apparent from theoretical consideration that an important case would be the limiting one on the lower side for which the axial force is zero. This involved merely determination of the central deflections of the column as a vertical beam under a single central load. The line passing through the points representing the relation of lateral deflection to lateral load when no axial load existed has been called the zero load line.

It was found convenient, in general, to relate the applied loads to the estimated Euler load, based on a length of 240 in., making them, for example, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, and $1\frac{1}{2}$ times that load. In all cases, at least one load below the Euler load, in addition to the zero load, was used.

For the purpose of computing the Euler load from Equation (1) of Part III, actual values of EI were determined from observations on the column acting as a vertical beam.

Although the deflections of the two flanges were not in general the same, all diagrams indicating the relation of lateral supporting force to axial load were so plotted that the deflection indicated on the horizontal scale is the deflection of the supported point, be it the middle of the web or the edge of a flange.

Centric load. For loads below the Euler load, in the case of a perfectly straight column, a lateral load had to be applied to produce deflection.

For the Euler load, the various deflections were produced without any appreciable change in the lateral force. This is in accordance with the theory of action of the Euler column.

For loads greater than the Euler load the column naturally deflected in the direction of the initial curvature or unavoidable eccentricity, and lateral force had to be applied to hold it to a desired deflection.

Eccentric loads. Eccentric loads were handled in the same manner as centric ones, with the exception that there was no tendency to take up natural deflection in a direction opposed to the eccentricity within the desired maximum deflection.

The plotted results for the earlier columns indicated that they were acting in a certain regular and definite manner. All lines representing axial loads intersected at a point on the zero load line. For eccentric loads this intersection point moved outward from the origin to the North or South, according as the eccentricity of loading was North or South. The amount of this movement was found to be approximately $\frac{4}{3}e$, where e is the eccentricity of application of the load. The lateral supporting force was, therefore, the same for all axial loads when the deflection was equal to this amount. From observation it appeared that the cylindrical end bearings were at their greatest distance apart at this deflection, since the loading head of the machine had to be lowered for deflections on either side of this point. Theoretical calculations later substantiated this belief.

III. Theoretical Considerations

5. *General*

Given a column with imperfections that may be readily represented mathematically, it is possible to develop expressions for the central transverse supporting load consistent with the axial load, the properties and peculiarities of the column, the eccentricity, and the deflection.

In the general case, allowance must be made for initial crookedness in the column. It is not practicable to take account mathematically of local kinks, but it is entirely feasible to include the effect of smooth initial curvature. Investigations have been made on the basis of three assumptions, namely, *(a)* that the initial curve is a sinusoid, or the deflection curve of a centrically loaded long column, *(b)* that it is parabolic, and *(c)* that it is the same as that for a simply supported beam subjected to a central transverse load.

6. *Euler Load, Ends Pivoted*

For centrically loaded, perfectly straight, homogeneous columns of such slenderness ratio that failure may occur by buckling before the elastic limit of the material is reached, the ultimate, or Euler, load is given by the formula

$$P_e = A \cdot \frac{\pi^2 E}{\left(\frac{l}{r}\right)^2} = \frac{\pi^2 EI}{l^2}, \tag{1}$$

in which A = area of the column;
E = modulus of elasticity of the material;
l = length of the column applicable to the direction of buckling;
r = radius of gyration in the direction of the buckling.

Within this load the column will remain perfectly straight; there will be no lateral deflection, no bending moment and, in theory, no need for lateral support. If the Euler load be exceeded ever so little the column will suddenly buckle sideways and collapse owing to form change, or springiness. The exact Euler load will hold the column at any deflection put in it by a lateral force temporarily applied and removed.

7. *Lateral Supporting Force for Eccentric Loading*

The lateral supporting force will be found by taking into account the actual curve produced in the column by the forces acting on it, evaluating in the one process the net effect of the force that the column by reason of its geometrical form tends to exert against a theoretical stop placed at mid-height and the spring-back effect. In certain instances a negative sign will be found associated with the lateral supporting force. This indicates that it is necessary to force the column out into the deflected position indicated by the application of a force Q in the sense of the bulge.

Since the natural crookedness of a column is irregular and unpredictable, the assumption that the initial curve is a sinusoid is as good as any other. If the deviation at the centre is c, then

$$z = c \sin \frac{\pi x}{l} \tag{2}$$

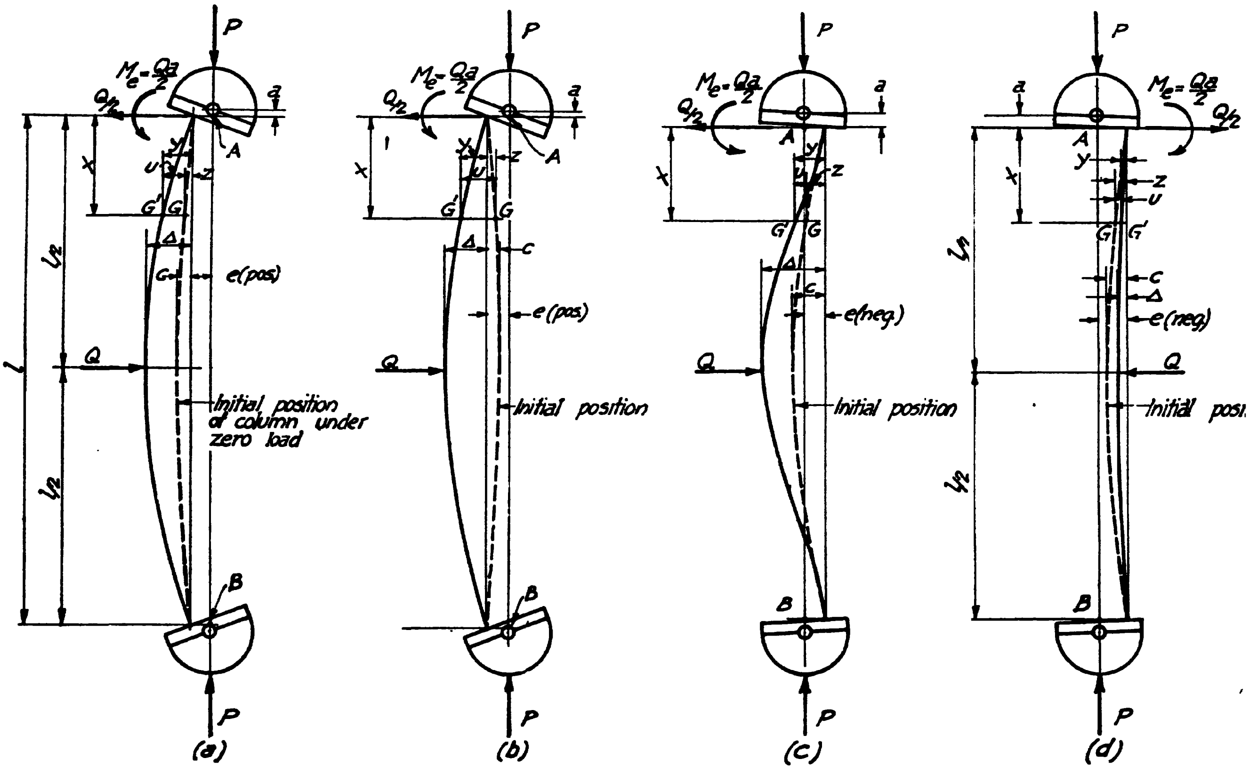


FIG. 5. *Lateral supporting force, Q, for columns subjected to eccentric axial lo*

Case (a). Consider the column shown in Fig. 5*(a)*. Any general point G on the unstressed column will move, under the system of applied forces, to G', or through a horizontal distance u. The distance y of the point G' from the straight line joining the ends of the column is thus made up in part of an initial no-stress deviation z and an elastic deviation or deflection u; that is,

$$y = u + z \tag{3}$$

The moment at the point G', if we count clockwise moments on the portion of the column above G' as positive, is

$$M = P(u + z + e) - \frac{Qx}{2} - \frac{Qa}{2} \tag{4}$$

Let the origin be at A, the point where a horizontal line through the end of the column shaft cuts the load line. Let x be positive when measured downward, and e, z, u, and y be positive if measured to the left. Then,

$$\frac{d^2u}{dx^2} = -\frac{M}{EI}.$$

Proceeding along the general lines of J. E. Boyd's analysis (1) and inserting the value of M from Equation (4), and z from Equation (2),

$$\frac{d^2u}{dx^2} + \frac{Pu}{EI} = -\frac{Pc}{EI}\sin\frac{\pi x}{l} - \frac{Pe}{EI} + \frac{Qx}{2EI} + \frac{Qa}{2EI} \tag{5}$$

Solving this equation, evaluating the constants, introducing the value of z given in Equation (2), and noting that when $x = \frac{l}{2}$, $y = \Delta$,

$$\Delta = \frac{\frac{c\pi^2}{l^2}}{\frac{\pi^2}{l^2} - \frac{P}{EI}} + \left(e - \frac{Qa}{2P}\right)\sec\sqrt{\frac{P}{EI}}\cdot\frac{l}{2}$$

$$- \frac{Q}{2P}\sqrt{\frac{EI}{P}}\tan\sqrt{\frac{P}{EI}}\cdot\frac{l}{2} - e + \frac{Ql}{4P} + \frac{Qa}{2P}. \tag{6}$$

Now, if for further simplicity we let $m = \sqrt{\frac{P}{EI}}$

$$\sqrt{\frac{P}{EI}}\cdot\frac{l}{2} = \alpha, \text{ and } \frac{\frac{c\pi^2}{l^2}}{\frac{\pi^2}{l^2} - \frac{P}{EI}} = rc,$$

and replace (sec α − 1) by exsec α, we may write finally for Case (a)

$$Q = \frac{2P\,(rc + e\,.\,\text{exsec}\,\alpha - \Delta)}{a\,.\,\text{exsec}\,\alpha + \frac{1}{m}\tan\alpha - \frac{l}{2}}. \tag{7}$$

Case (b). As is evident from Fig. 5*(b)* the only difference between Case *(a)* and Case *(b)* is that the initial crook is opposite in sense to the deflection Δ. Equation (7) is, therefore, applicable if a negative sign is attached to the first term in the numerator and the arithmetic value of c is employed. We then have

$$Q = \frac{2P(-rc + e\,.\,\text{exsec}\,\alpha - \Delta)}{a\,.\,\text{exsec}\,\alpha + \dfrac{1}{m}\tan\alpha - \dfrac{l}{2}}. \tag{8}$$

Case (c). Except for negative eccentricity, Case *(c)* is the same as Case *(a)*. Introducing the negative sign for the second term in the numerator of Equation (7), and using the arithmeric value of e, there results

$$Q = \frac{2P(rc - e\,.\,\text{exsec}\,\alpha - \Delta)}{a\,.\,\text{exsec}\,\alpha + \dfrac{1}{m}\tan\alpha - \dfrac{l}{2}} \tag{9}$$

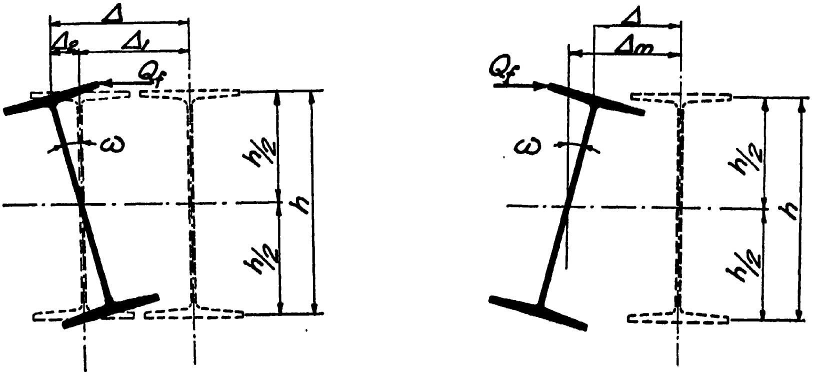
Case (d). Case *(d)* is analogous to Case *(c)* in that the sense of c, e, and Δ is relatively the same. Equation (9) consequently applies. The sense of the lateral supporting force will depend on the relative values of the three terms in the numerator.

8. *Force Required to Produce a Given Deflection of a Flange when Applied in Its Plane, and with Zero Axial Load*

Preliminary to a consideration of the lateral supporting force required for an axially loaded column when the force is applied at the edge of a flange, and parallel thereto, rather than at the middle of the web, it is desirable to ascertain the relation between a force applied to a flange and the resulting deflection of that flange, P being zero.

The total deflection of the loaded flange of a straight column, as indicated in Fig. 6*(a)*, is

$$\Delta = \Delta_1 + \Delta_2\,, \tag{10}$$



(a) (b)

FIG. 6. *Relation of mean deflection to deflection of loaded flange.*

where Δ_1 = deflection if the lateral force Q were applied at the middle of the web of the column, and,

Δ_2 = additional deflection due to the torque, which arises from the application of Q_f at a flange centroid, that is, at $h/2$ from the centre of the cross section.

For a transverse force Q_f applied at mid-height of a column of length l, with perfectly hinged ends, the centre deflection is

$$\Delta_1 = \frac{Q_f l^3}{48EI}. \tag{11}$$

As is evident from Fig. 6 *(a)*, the added deflection at the loaded flange due to the torque is

$$\Delta_2 = \omega \cdot \frac{h}{2},$$

the angle ω being the total twist angle developed in the half length, $l/2$, of the column.

Now, under the constant torque, T, existing in the half length, this twist angle is

$$\omega = \frac{Tl}{2E_s J}, \tag{12}$$

where E_s = shearing modulus of elasticity, and,

J = torsional stiffness factor, which may be determined by experiment or, approximately, by empirical formula.

Values of J for the various sections tested were computed by the method of Lyse and Johnston (2).

For a torque applied at mid-length of a column, the torque in either half length is

$$T = \frac{Q_f}{2} \cdot \frac{h}{2} = \frac{Q_f h}{4},$$

where h is the distance between flange centroids. The twist angle at mid-length becomes, therefore,

$$\omega = \frac{Q_f hl}{8E_s J}, \tag{13}$$

and it follows that

$$\Delta_2 = \frac{Q_f h^2 l}{16E_s J}. \tag{14}$$

Substituting in Equation (10) the values of Δ_1 and Δ_2 obtained from Equations (11) and (14) and solving,

$$Q_f = \frac{48EI\Delta}{l^3 + \frac{3EIh^2 l}{E_s J}}. \tag{15}$$

The effect of the torsion is obviously represented by the second term in the denominator.

9. Lateral Supporting Force Required for Axially Loaded Column when Applied at Flange Centroid

When a lateral supporting force holds a flange at a deflection Δ, while the mean deflection of the cross section is Δ_m, Fig. 6*(b)*, the amount of work that has had to be done by it is the same as the amount that would have to be done by a force applied at the middle of the web and holding the whole cross section to a deflection of Δ_m. This is true because the moment and deflection effects produced by the advanced position of one-half of the section beyond Δ_m are offset by the effects of the equally retarded position of the other half.

Experiment confirms this. Studies of the relative lateral supporting forces for flange-supported and web-supported columns show that with flange support the lateral supporting force for a given mean deflection equals the lateral supporting force for a web-supported column with a deflection equal to the mean for the flange-supported one.

If, then, the mean deflection could be found or predicted, it would be possible to utilize, for flange support, formulae and diagrams for web-supported columns, employing mean deflections in all cases.

As Δ_m is not known beforehand, it is desirable to express it in terms of a known deflection, that is, Δ.

Now, the mean deflection for the case of positive lateral supporting force, Q_f, Fig. 6*(b)*, is

$$\Delta_m = \Delta + \frac{Q_f h^2 l}{16 E_s J}. \tag{16}$$

If it should happen that the axial load is such that lateral force has to be exerted to cause the column to move out to the desired deflection, Q_f becomes negative and the mean deflection is less than Δ.

Since the lateral supporting force for a flange-supported column equals the lateral supporting force for a web-supported column with a deflection Δ_m, the latter may be inserted as the value of Δ in Equation (7). Then

$$Q_f = \frac{2P(rc + e\,.\,\mathrm{exsec}\,\alpha - \Delta_m)}{a\,.\,\mathrm{exsec}\,\alpha + \dfrac{1}{m}\tan\alpha - \dfrac{l}{2}}.$$

Inserting the value of Δ_m from Equation (16), and letting the denominator be represented by D, we have

$$Q_f = \frac{2P(rc + e\,.\,\mathrm{exsec}\,\alpha - \Delta)}{D} - \frac{PQ_f h^2 l}{8DE_s J}.$$

The first term of the right-hand member of this equation is obviously equal to the support necessary for a web-supported column with deflection equal to Δ, the deflection imposed upon the supported flange of the flange-supported column. Letting this term be Q_w, there follows

$$Q_f = \frac{Q_w}{1 + \dfrac{Ph^2 l}{8DE_s J}}. \tag{17}$$

Equation (17) relates the desired flange force to the web force necessary to maintain a mean deflection in the section equal to any arbitrarily selected deflection for the supported flange.

IV. Analysis of Results

10. General

The principal test results were set out for consideration in 20 diagrams, of which Fig. 7, relating to column 9*A*, is typical. These showed the relation between applied lateral force, deflection, and axial load on the column for both centric and eccentric loads and for lateral support applied either to the middle of the web or to the edge of a flange. The deflection indicated on the horizontal scale is the deflection of the supported point, as indicated in Fig. 6. Fig. 8 gives the characteristic relation of the lateral force to varying axial load for columns *C1A* to *C4B*. Figs. 9, 10, 11, and 12 indicate the nature of the column curvature for the columns when the deflection of either the web or a flange at mid-height of the column is held at zero.

11. Comparison of Theoretical with Experimental Results

It was thought desirable to indicate on the lateral-force–deflection diagrams, such as Fig. 7, certain points that would lie on the theoretical lines of lateral-force–deflection, but, to avoid confusion, these lines have not been drawn in. The points are indicated for an approximate theory, as represented by the equations

$$Q = \frac{4.87P(\Delta + 1.23e)}{l} - \frac{48EIn}{l^3} \tag{18}$$

and

$$Q_f = \frac{Q_w}{1 + \dfrac{h^2 l}{16E_s J}\left\{\dfrac{48EI}{l^3} - \dfrac{4.87P}{l}\right\}}, \tag{19}$$

where n = the central deflection of the column from its unstrained position, and for the so-called exact theory, as represented by Equations (7) and (17). The first right-hand term of Equation (18) represents the approximate value of the force that the column by reason of its geometrical properties only would bring to bear against an imaginary stop placed against it at mid-height, and the second term, the spring-back effect due to the elastic properties of the column. Points have also been indicated on the lines that would be drawn in the construction of the Jackson diagram, the nature of which is described in Art. 12.

In plotting the points for these theoretical lines it was necessary to place the origin in such a position as to take account of any accidental or unpredictable eccentricity effects that may have been revealed by the tests but for which no allowance is made in the formulae.

12. Jackson Diagram

An interesting method of determinating the necessary lateral supporting force for a column subjected to centric or eccentric loading is available through the construction of a diagram proposed by Prof. K. B. Jackson and later

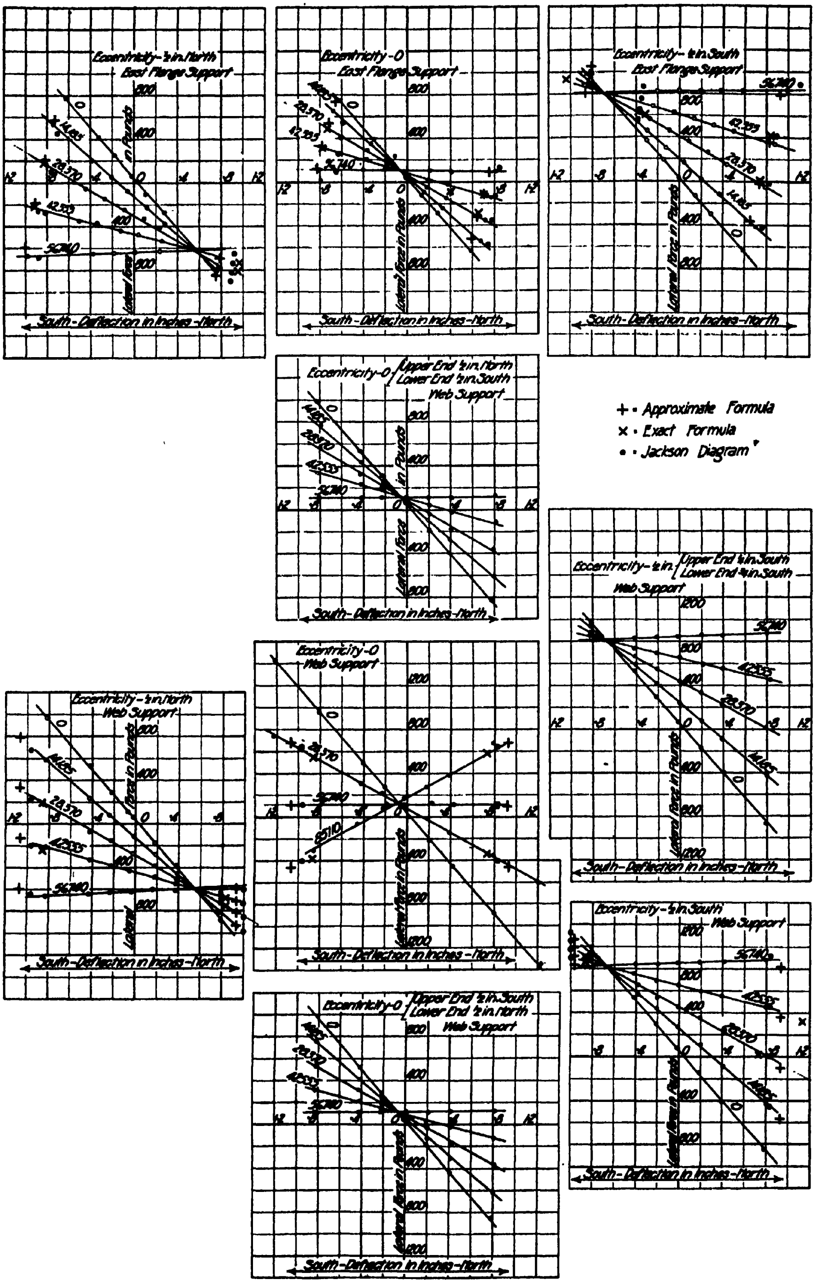


FIG. 7. *Lateral-force–deflection diagrams for Column C9A.*

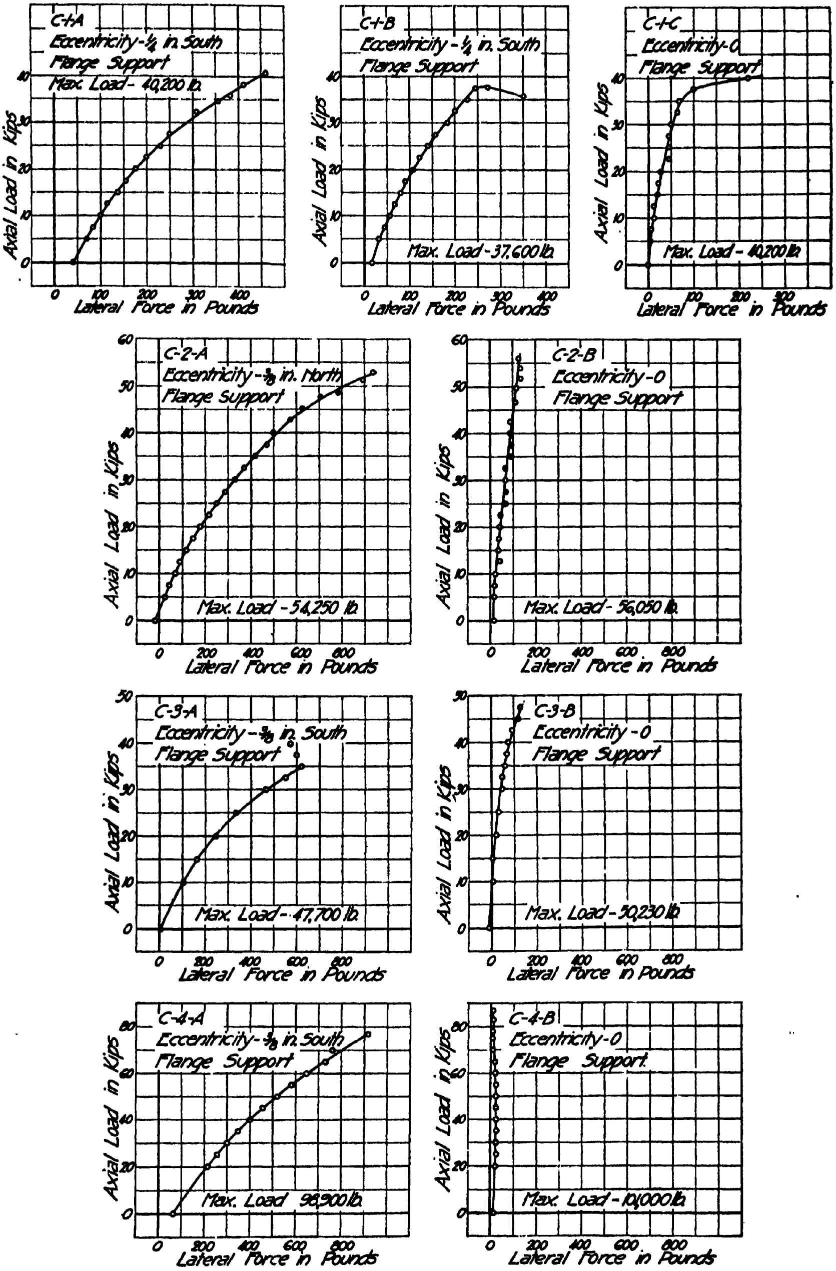
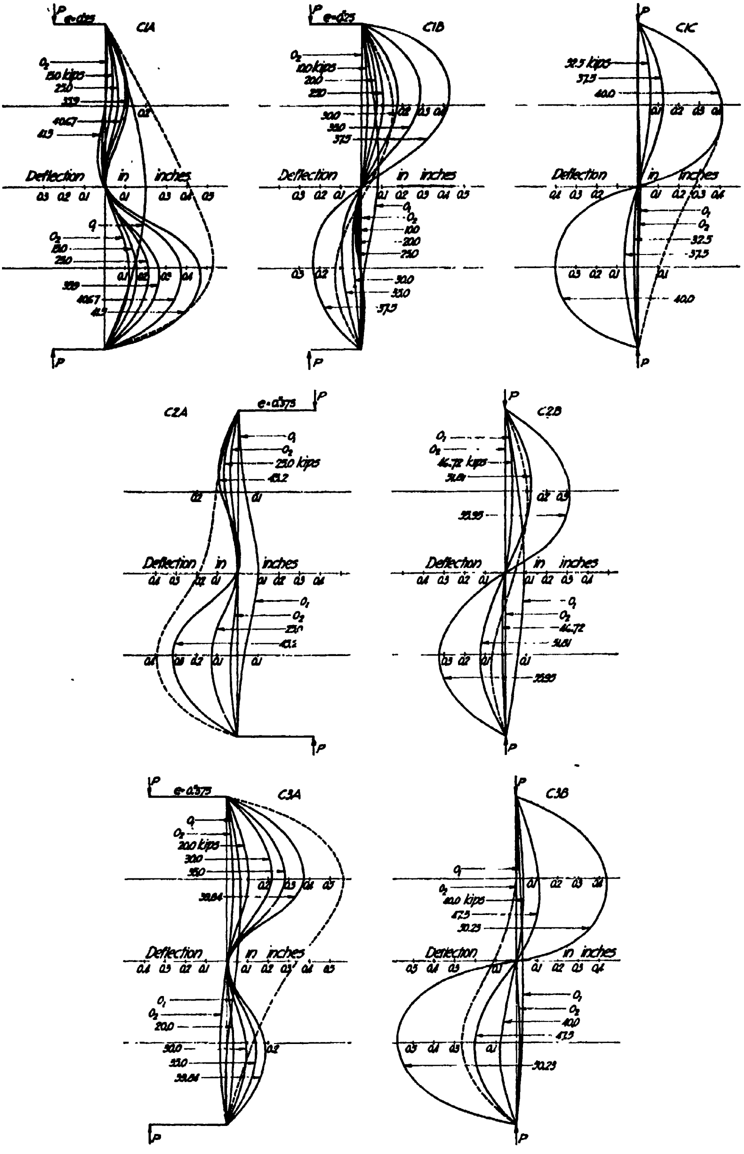
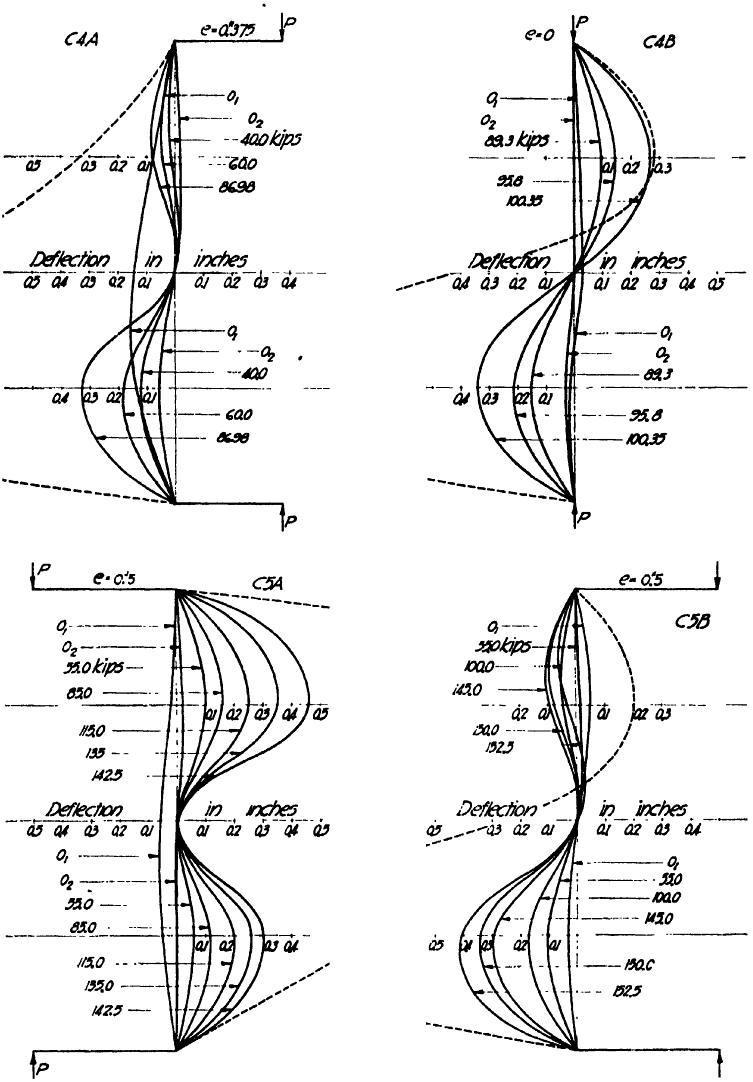


FIG. 8. *Observed relation of lateral force to axial load for columns C1A to C4B to maintain zero deflection at point of support.*



Note:-
The axial load corresponding to each deflection curve is indicated in kips.
O_1 indicates the form of the unloaded column.
O_2 indicates the form of the column under zero axial load, when the mid-point of the flange is forced to lie on the line joining the ends of the column shaft.
The broken line indicates permanent deformation.

FIG. 9. *Observed deflections of East flange of columns C1A, C1B, C1C, C2A, C2B, C3A, and C3B for mid-height deflection of zero at East flange.*



NOTE:-

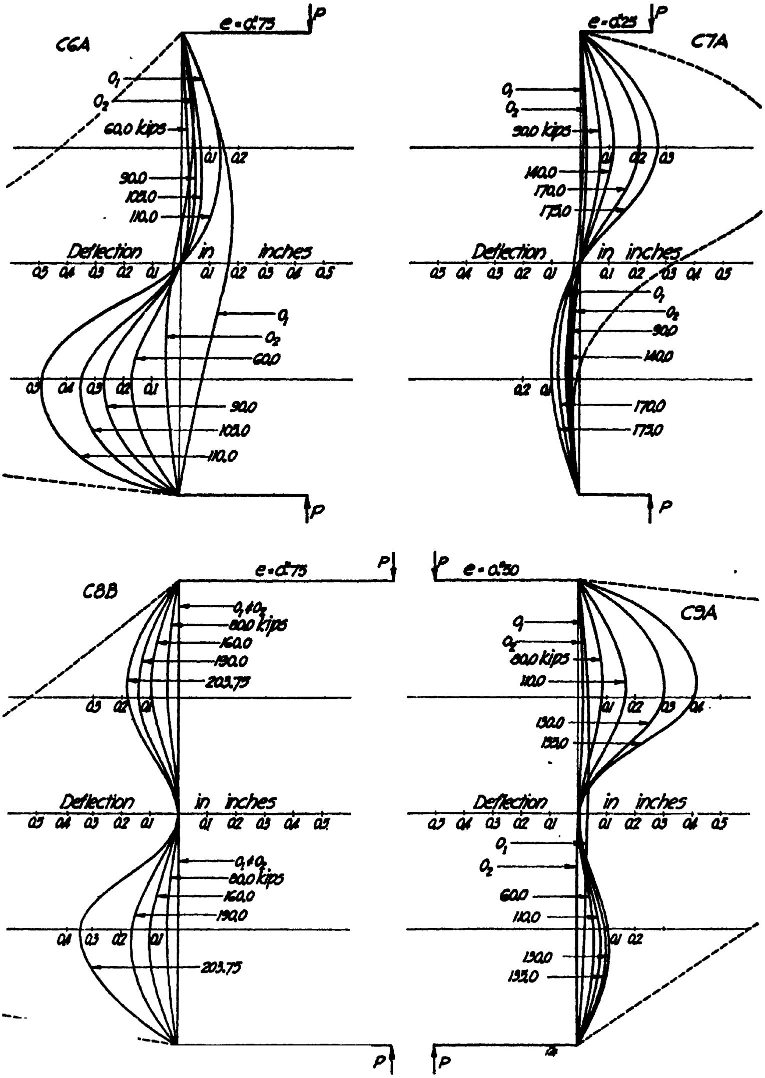
The axial load corresponding to each deflection curve is indicated in kips.

0_1 indicates the form of the unloaded column.

0_2 indicates the form of the column under zero axial load, when the mid-point of the flange is forced to lie on the line joining the ends of the column shaft.

The broken line indicates permanent deformation.

FIG. 10. *Observed deflections of East flange of columns C4A, C4B, C5A, and C5B for mid-height deflection of zero at East flange.*



NOTE :-

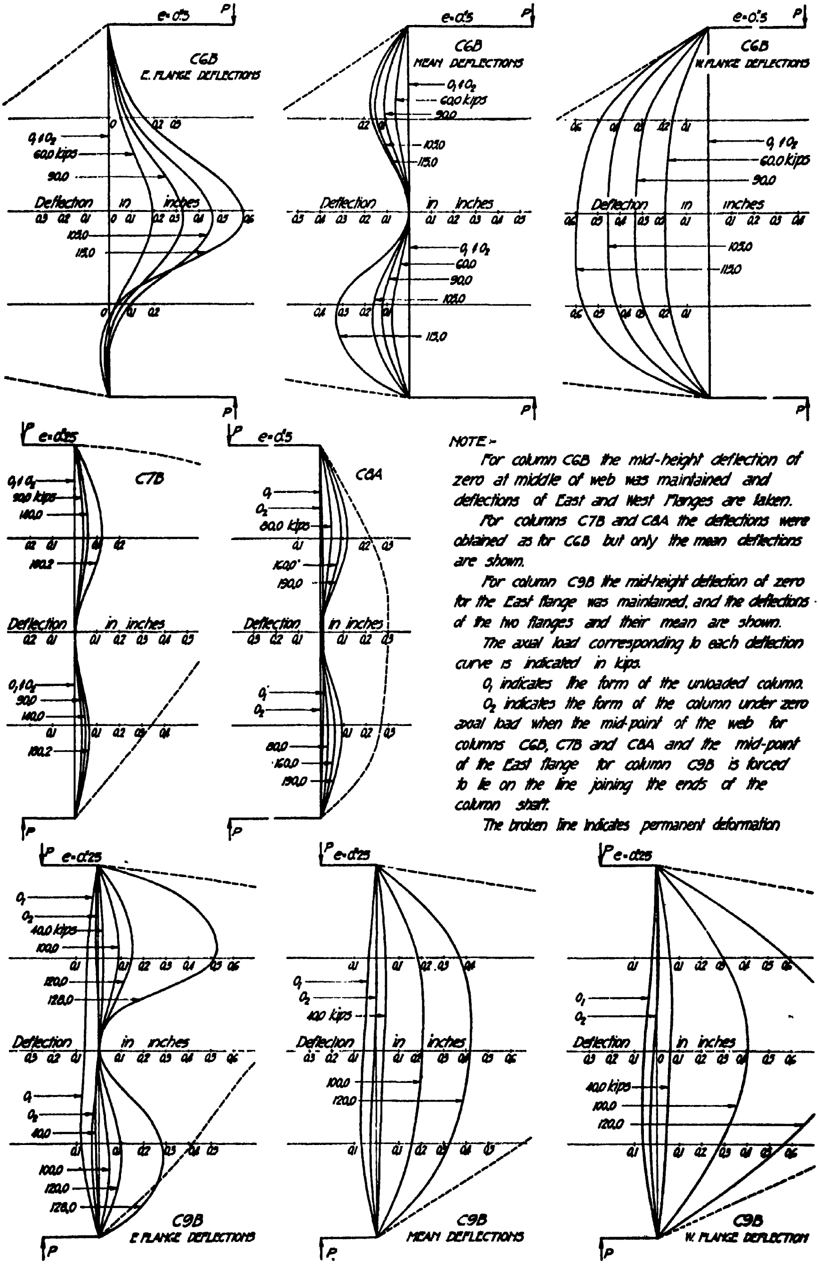
The axial load corresponding to each deflection curve is indicated in kips.

O_1 indicates the form of the unloaded column.

O_2 indicates the form of the column under zero axial load, when the mid-point of the web is forced to lie on the line joining the ends of the column shaft.

The broken line indicates permanent deformation.

FIG. 11. *Mean deflections of flanges of columns C6A, C7A, C8B, and C9A for mid-height deflection of zero at middle of web.*



NOTE:-

For column C6B the mid-height deflection of zero at middle of web was maintained and deflections of East and West Flanges are taken.

For columns C7B and C8A the deflections were obtained as for C6B but only the mean deflections are shown.

For column C9B the mid-height deflection of zero for the East flange was maintained, and the deflections of the two flanges and their mean are shown.

The axial load corresponding to each deflection curve is indicated in kips.

O_1 indicates the form of the unloaded column.

O_2 indicates the form of the column under zero axial load when the mid-point of the web for columns C6B, C7B and C8A and the mid-point of the East flange for column C9B is forced to lie on the line joining the ends of the column shaft.

The broken line indicates permanent deformation

FIG. 12. *Deflections of columns C6B, C7B, C8A, and C9B.*

adapted to take into account natural or initial crook. A column will be considered with a crook, c, but with no accidental errors.

Modifying Equation (18) to conform to the results of experiment, by replacing $1.23\,e$ by $1.33\,e$, we have

$$Q = \frac{4.87P}{l}(\Delta + 1.33e) - \frac{48EIn}{l^3}. \qquad (20)$$

It is necessary to find first the slope of the zero axial load line, 0–0. When $P = 0$, Equation (20) becomes

$$Q = \frac{48EIn}{l^3}.$$

If now

$$n = \frac{l}{4.87X},$$

where X = the ratio of the axial load as indicated by the height of any selected point on the vertical axial load scale to the lateral supporting force indicated by the height of the same point on the lateral load scale, or the ratio of the scales, then

$$Q = \frac{48EI}{l^3} \times \frac{l}{4.87X} = \frac{1}{X} \cdot \frac{\pi^2 EI}{l^2}$$

$$= \frac{1}{X} \times \text{Euler load for the column.}$$

Now, as indicated in Fig. 13, lay off $O'A = n = \Delta - c = \frac{l}{4.87X}$ to the left from the point O' where $OO' = c$, the initial crook of the column, if any. The point O' may be to the right or left of the origin O, depending on the direction of the crook.

From A erect a vertical AB equal to the Euler load on the axial load scale, or $\frac{1}{X}$ times the Euler load, according to the lateral force scale. Join BO' and produce. This gives 0–0, the zero axial load line.

Next, erect a vertical $O'C$ through O' and lay off on it the various axial loads to be considered, e.g., $O'C$ = 60,000 lb. Join BC.

Lay off $\Delta = OD = \frac{4}{3}e$ from the original vertical axis, to the left if the eccentricity is to the South, or to the right, if it is to the North. Erect a vertical DE cutting 0–0 at E. E will be the point of intersection of load lines for an eccentricity of e to the South. Draw EF parallel to BC. EF will be the 60,000 lb. load line.

For any assumed deflection Δ from the vertical axis through O, that is, through the ends of the column, the corresponding vertical height to EF gives the necessary lateral supporting force applied symmetrically to the width of the column, or what has been called web support. For example, for a deflection of OG to the North, the lateral supporting force is GW.

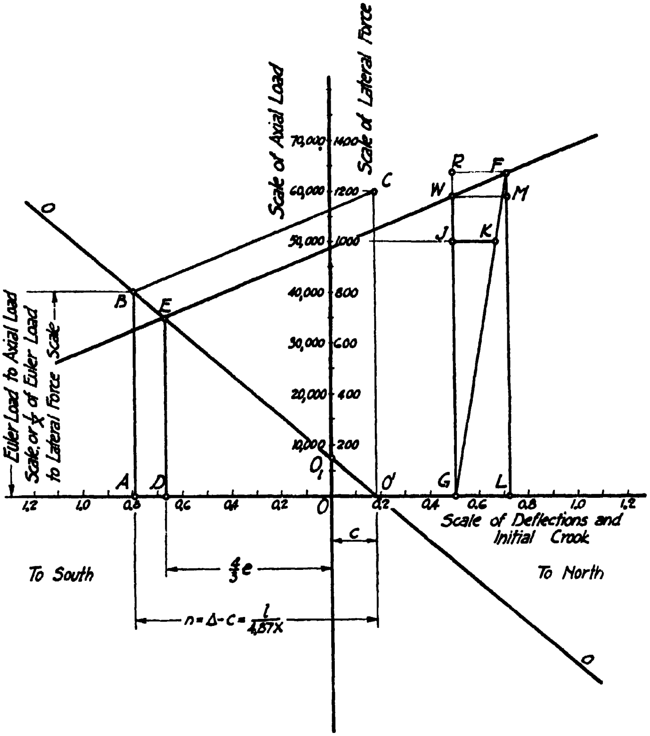


FIG. 13. *Construction of Jackson diagram.*

If the column were supported on the edge of a flange, the lateral force necessary to hold the flange to a deflection of *OG* will be increased. The method of determining this lateral force for flange support and for a flange deflection of, say, *OG* is as follows:

Estimate from the known torsional characteristics of the section considered the amount of torsional displacement Δ_t of a flange under an applied load $Q_f = 1000$ lb. at the edge of the flange and in its plane. Lay off $GJ =$ 1000 lb. and $JK = \Delta_t$. Produce *GK* to *F*. Then, the height *LF* gives the lateral support required for a deflection $\Delta = OG$ of the supported flange if the support is at the flange edge. Its excess over the required web support is *MF*.

13. Value of Lateral Support

Table II indicates the increase in ultimate strength of a hinged column laterally supported at mid-height without applied rotational restraint over the strength of a corresponding column without intermediate lateral support of any kind.

The ultimate test load of each column is compared with *(a)* the theoretical Euler load for zero eccentricity, Equation (1), based on a length of 240 in.,

TABLE II

RELATION OF OBSERVED ULTIMATE STRENGTH OF THE TEST COLUMNS TO THEORETICAL STRENGTH

NOTES: (1) Eccentricity of loading was in every case normal to the plane of the web. N = North eccentricity, that is, the axial load was applied to the North of the gravity axis of the column. S = South eccentricity.

(2) Ultimate loads were applied with the lateral support at the edge of one flange, except for specimen *C9A*, for which the lateral support was provided at the centre of the web.

(3) E = 29,000,000 lb. per sq. in.

Column mark	Eccentricity of ultimate test load at end of column, in.	Ultimate test load, lb.	Theoretical ultimate load by Formula (21) for full-length crooked column, lb.	Theoretical Euler load (zero ecc'y) for $l = 240$ in., lb.	Slenderness ratio $\frac{l}{r}$ for $l = 240$ in.	Ratio of (3) to (5)	Ratio of (3) to (4)	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
C1A	0.25 S	42,000	8,620	9,840	353	4.27	4.87	Continuity moment
C1B	0.25 S	35,490	9,350	10,350	353	3.43	3.80	
C1C	0	40,200		10,060	353	3.99		
C2A	0.375 S	48,050	13,690	15,500	324.3	3.10	3.51	Continuity moment
C2B	0	52,800	14,100	14,680	324.3	3.59	3.75	
C3A	0.375 S	47,700	11,700	13,440	303.9	3.55	4.07	Continuity moment
C3B	0	50,400		13,440	303.9	3.75		
C4A	0.375 N	98,900	22,100	26,610	272.9	3.71	4.47	Continuity moment
C4B	0	101,000		26,610	272.9	3.79		
C5A	0.50 S	145,000	36,900	45,000	237.7	3.22	3.93	Continuity moment
C5B	0.50 N	152,500	37,200	45,300	237.7	3.37	4.10	Continuity moment
C6A	0.45 N	110,500	34,200	39,800	208.7	2.78	3.23	
C6B	0.56 N	116,200	30,200	38,850	208.7	3.02	3.84	Continuity moment
C7A	0.25 N	178,200	60,000	71,000	184.6	2.51	2.97	
C7B	0.23 S	180,200	60,800	70,300	184.6	2.56	2.96	Continuity moment
C8A	0.53 S	207,000	72,600	102,800	156.9	2.02	2.85	Continuity moment
C8B	0.77 N	203,750	65,800	102,800	156.9	1.98	3.10	Continuity moment
C9A	0.50 S	139,500	41,600	54,400	206.9	2.56	3.35	Continuity moment
C9B	0.25 S	129,100	47,800	53,200	206.9	2.43	2.70	Continuity moment

the distance between the end pivots, and *(b)* the theoretical ultimate load by the commonly employed secant formula

$$P = A \cdot \frac{f_y}{1 + \frac{ey_1}{r^2} \sec \frac{l}{2}\sqrt{\frac{P}{EI}}}, \tag{21}$$

in which f_y = compressive yield point of the steel, taken for all columns as 36,000 lb. per sq. in.;

e = eccentricity of load with respect to the column axis at mid-height, that is, including the effect of crook;

y_1 = distance from column axis to extreme fibre of column section in the plane of bending;

r = radius of gyration;

l = theoretical length of column;

E = modulus of elasticity of the material;

I = moment of inertia of the column in the direction of bending.

Three major influences affect the extent of the improvement in strength: *(a)* the slenderness ratio of the column; *(b)* the eccentricity of the loading; and *(c)* the existence of continuity moment at mid-height.

With equal eccentricities of the same sign at the two ends the column tends to bend in the same direction in the upper and lower halves and thus to develop continuity moment at the middle support. This was found to exist in most eccentrically loaded columns, as is apparent in Table II. But, doubtless owing to some accidental and unpredictable irregularities, the bending was opposite in sense in the two halves for columns *C1B*, *C6A*, and *C7A*. With zero eccentricity the nature of the buckling is unpredictable. Figs. 9 to 12, inclusive, show the form of the bending.

In column (7) of Table II is indicated the ratio of the ultimate test load to the theoretical Euler load calculated on the assumption that no intermediate lateral support existed. This ratio varies from 1.98 for specimen *C8B*, which is one of those having the lowest slenderness ratio, to 4.27 for *C1A*, which is one of those having the highest slenderness ratio. The eccentricity for the first-mentioned column was larger than that for any of the other columns, and for the last-mentioned it is one of the smallest for the eccentrically loaded columns. Continuity moment at mid-height existed for both of these extreme cases.

While the load stages were based on the Euler load and a comparison of the ultimate test load with it has been made, it is obvious that the calculated Euler load has but slight significance for columns with eccentricity of loading. Comparison of the test load with the ultimate load computed by the secant formula is, however, valid.

Column (8) of Table II indicates that the ultimate test load related to the ultimate load as calculated by the secant formula gave ratios ranging from 2.7 for column *C9B* to 4.87 for column *C1A*. The slenderness ratio ranged, respectively, from the third lowest value to the highest value. The eccentricities were the same and continuity moment existed in both cases.

Table II indicates that, as might be expected, the benefit of lateral support tends to be least for columns having the lowest values of the slenderness ratio. There appears to be no clear-cut and consistent law discernible from the tests respecting the relation of the benefit of lateral support to the eccentricity.

It is, however, useful to know that for columns with eccentricity up to one-eighth of the column width the furnishing of lateral support at mid-height of the column increases the strength to from 2.70 to 4.87 times the theoretical strength of the full-length column as computed by the secant formula.

14. Recommended Values for the Lateral Supporting Force for Web Support

Examination of the relation of the experimental lateral-force–deflection lines to the plotted theoretical points for all the columns showed that the plotted points for the approximate formulae of Equations (18) and (19), for the so-called exact formulae of Equations (7) and (17), and for the Jackson diagram conform fairly well to the experimental curves, except in the cases of

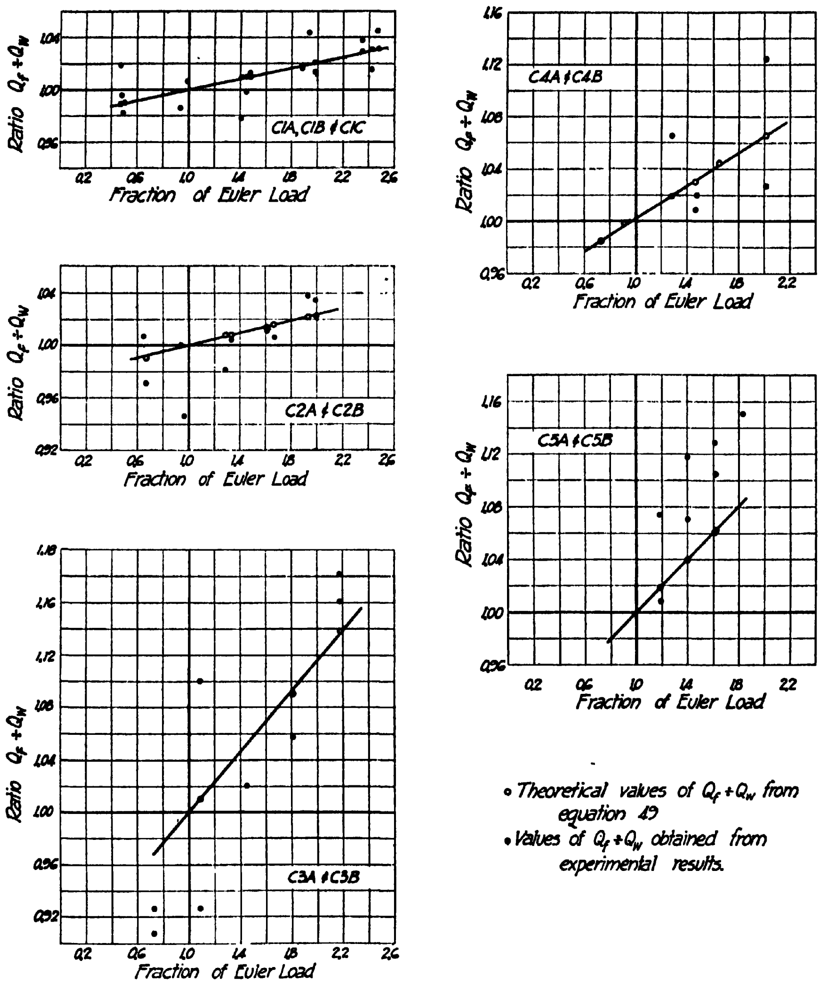


FIG. 14. *Comparison of theoretical and experimental values of the ratio $Q_f \div Q_w$.*

the larger axial loadings. As is evident from Fig. 8, the ratio that the lateral force Q bears to the axial load P to maintain zero deflection at the point of support increases somewhat with the load. There is no reason to suppose that the variation would be markedly different if some deflection were permitted at the point of support.

Various adjustments of the proposed formulae for the value of the lateral supporting force were tried in order to give greater weight to the magnitude of the axial force, some involving exponential functions. On the whole, the most satisfactory one resulted from a slight modification of Equation (20),

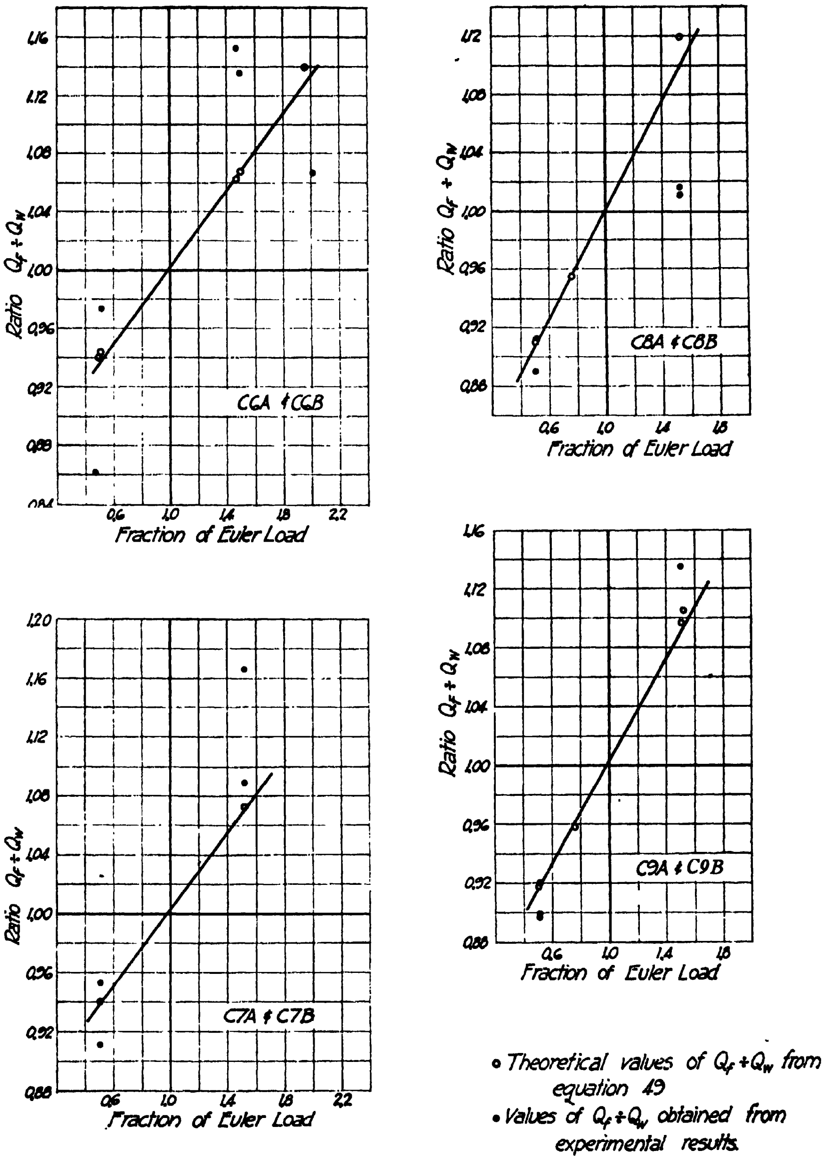


FIG. 15. *Comparison of theoretical and experimental values of the ratio $Q_f \div Q_w$.*

giving as the recommended working formula for the lateral supporting force, where the support is at the middle of the width of the section,

$$Q_w = \frac{5P}{l}(\Delta \pm 1.33e) - \frac{48EIn}{l^3} \qquad (22)$$

The plus sign is to be used in the first term of Equation (22) when the end eccentricity is on the side of the straight line joining the column ends opposite to that on which the deflected column axis lies. The negative sign applies when the deflected axis and the end eccentricity are on the same side.

15. Relation of Lateral Supporting Force for Flange Support to That for Web Support

The relation between the magnitude of the lateral supporting force when applied at the edge of the flange and the necessary force when it is applied at the middle of the web is given approximately by Equation (19) and more rigorously by Equation (17). The ratios given by the latter formula, based on the relation of the axial load to the Euler load for the column, are plotted on diagrams giving the observed values of the ratios in Figs. 14 and 15.

A simplified variant of Equation (19) was found to give results that were on the whole quite as satisfactory as those given by either Equation (19) or Equation (17). It is

$$Q_f = \frac{Q_w}{1 + \frac{h^2 l}{E_s J}\left(\frac{3EI}{l^3} - \frac{P}{3l}\right)} . \qquad (23)$$

Acknowledgments

The authors are greatly indebted to the National Research Council and to the School of Engineering Research of the University of Toronto for financial assistance received in connection with the work. Without this, the investigation would have been impossible.

Acknowledgment is here made (in alphabetical order) of the able and conscientious services of R. I. P. Barnes, H. St. Paul Butler, C. E. Helwig, G. V. Helwig, K. B. Jackson, P. V. Jermyn, and C. F. Morrison. The authors are particularly indebted to Prof. K. B. Jackson for many ingenious and valuable suggestions in connection with various aspects of the work.

References

1. BOYD, J. E. Trans Am. Soc. Mech. Engrs. 51(10) : 93-103. 1929.
2. LYSE, Inge and JOHNSTON, B. G. Trans. Am. Soc. Civil Engrs. 101 : 857-896. 1936.
3. YOUNG, C. R. Eng. News-Record, 123 (15) : 66. 1939.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. A. SEPTEMBER, 1942 NUMBER 9

ON THE ADSORPTION OF WATER VAPOUR BY CELLULOSE[1]

By J. D. Babbitt[2]

Abstract

In this paper an attempt is made to gather together the best available data on the adsorption of water vapour by cellulose and to draw from this data a unified picture of the phenomenon. In the first place the various theories explaining the adsorption isotherm are tested. The Langmuir isotherm is shown to fit a small portion of the curve at low relative humidities, and the polymolecular theory of Brunauer, Emmett, and Teller is found to give agreement up to the point where capillary adsorption is assumed to become predominant. It is pointed out, however, that the assumptions involved in the theory of Brunauer, Emmett, and Teller are such that an equally satisfactory agreement might be obtained by assuming that the adsorption was confined to a monomolecular layer in which, owing to repulsive forces between neighbouring atoms, the adsorbing force varied with the number of atoms. Thus it is still doubtful whether the adsorption is monomolecular or polymolecular. The investigation shows that the adsorption on cotton is similar to that on wood, except for the fact that the internal surface area available for adsorption is less by a factor of 1.86.

An analysis is made of the data available for calculation of the heats of adsorption, and the values obtained from the different sources are compared. It is found that when the heats of adsorption are plotted against the relative humidity there is no appreciable difference between the values obtained with cotton and with wood. A mean value for the heats of adsorption is obtained. The relation between heats of adsorption and the latent heat of condensation is developed, and it is shown that there is an excess of internal energy in the adsorbed state over that of the liquid state.

Finally, an explanation is advanced to account for the experimental fact that there is a reduction in total volume when water vapour is adsorbed on cellulose. An attempt is also made to show (i) how the water molecule may be attached to the cellulose surface by hydrogen bonds in such a way that the energy will be greater than that in liquid water, and, (ii) that, on the basis of such a picture a volume contraction is to be expected.

The nature of the relation existing between cellulose and those molecules of water vapour that are adsorbed on its surface is not only of great practical importance in the paper and cotton trades, but a knowledge of it is fundamental for a proper understanding of the phenomenon of adsorption. The adsorption isotherm is, in this case, of the familiar sigmoid shape that is found for a large variety of materials. In particular it is especially interesting that protein substances such as hair, wool, wheat, etc., adsorb water vapour in this manner, so that it is justifiable to believe that the same mechanism of adsorption is involved and that any explanation obtained for adsorption by cellulose would also hold for this large and important group of substances.

---

[1] *Manuscript received in original form April 28, 1942, and as revised, July 21, 1942.*

Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1076.

[2] *Physicist.*

Yet at present, even though a vast quantity of experimental work has been done it is impossible to explain adequately the most elementary facts about this relation, and even such fundamental datum as the absorption isotherm itself has not been satisfactorily derived from a theoretical point of view; the cause of the sigmoid shape of this isotherm and of the pronounced hysteresis effect are to be considered the subject of conjecture rather than the consequence of an established theory. There are numerous isolated data that have so far refused to fit into any general treatment. It is hoped in this paper to discuss a few of these facts and, to some extent, to weld them into a co-ordinated theory.

One of the great difficulties involved in any study of the adsorption of water on cellulose is the fact that all cellulosic materials are microscopically porous bodies, and it is impossible to estimate from a priori considerations the area of surface that plays a part in the phenomenon. This is a serious drawback, as it prevents any simple calculation of the area of surface available per adsorbed molecule, and hence eliminates the most direct method by which monomolecular may be distinguished from polymolecular adsorption. It is therefore impossible to apply to adsorption by cellulose the methods of study by which Langmuir and others have so successfully attacked the problem of adsorption by certain metals. However, the fact that with cellulosic materials a large indefinite surface is involved has the advantage that the adsorption is correspondingly large, so that simple gravimetric methods are available for determining the adsorption equilibrium.

It has become apparent during the past few years that the concept of monomolecular adsorption developed by Langmuir is not adequate to explain completely the adsorption isotherm for an adsorption of this nature. It does appear as though the curve for the first few per cent of moisture adsorbed can be made to fit a Langmuir equation, but there is no tendency for that saturation at high pressures that is characteristic of Langmuir adsorption. On the other hand, there is reason to believe that the rapid increase of the adsorption at relative humidities approaching saturation is caused by capillary condensation. It is the section of the isotherm between these two regions that is interesting, for it is obvious that here simple monomolecular adsorption is not adequate, while the radius of the capillaries required for capillary condensation is so close to the actual diameter of a molecule that it is absurd to think of applying the Kelvin expression to this region.

Recently a theory has been put forward by Brunauer, Emmett, and Teller (5) that explains the sigmoid-type isotherm by assuming that the adsorption is not confined to a monomolecular layer but that it takes place in the second, third, and higher layers. By applying Langmuir's equation successively to these layers and summing, an equation is obtained that fits the curve very satisfactorily up to relative humidities where capillary adsorption becomes predominant. They assume that the cause of the sigmoid curve is polymolecular adsorption superimposed on a monomolecular layer developed at low pressures according to Langmuir's conceptions, and at high pressures rapidly changing over to capillary condensation. There is some evidence, which will be outlined later, that the mechanism of polymolecular adsorption is not essential to explain adsorption of this nature, but Brunauer, Emmett, and Teller's theory will be developed on this basis and applied to cellulose in order to obtain a comparison with the experimental facts.

The Adsorption Isotherm

A typical adsorption isotherm for cellulosic materials is reproduced in Fig. 1. This has been taken from the measurements of Filby and Maass (10) and refers to white spruce wood at a temperature of 20° C. Both the adsorption and the desorption curves are given here and the hysteresis may be plainly seen. Curves of similar shape have been found for wood pulp, cotton, pure cellulose, wool, and in fact are common to all cellulosic materials and other swelling gels. This type of curve is not confined to those cases in which the adsorbate is water. Sigmoid curves are also found for the adsorption of various gases such as nitrogen, oxygen, argon, carbon monoxide, carbon dioxide, and butane (5), and the fact that such curves are found for all these gases immediately indicates that the explanation of the adsorption of water vapour by cellulose cannot be obtained from any special properties of the water molecule (such as its strong dipole moment). This also follows from the fact that when alcohols are adsorbed by wood, a curve of similar shape is obtained (17).

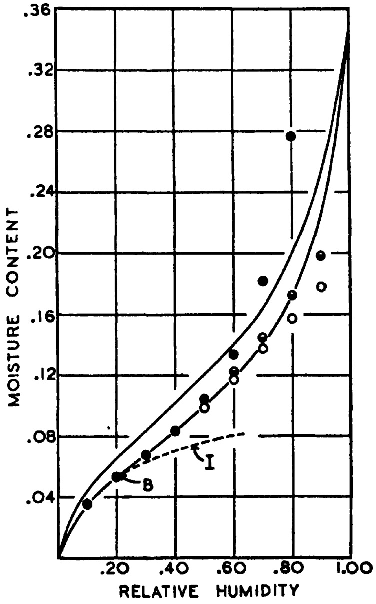


FIG. 1. *Adsorption isotherm for spruce wood. Full lines, experimental data of Filby and Maass. I, Langmuir's equation. Points, Brunauer's equation;* ●, *n* = ∞ ; ○, *n* = 6; ◒, *n* = 7.

Before developing the theory of polymolecular adsorption, it is interesting to study the simple Langmuir theory and to ascertain its possibilities and limitations. Langmuir's assumptions are that adsorption is confined to definite points of attraction on the adsorbing surface and that the adsorption is limited to a single molecular layer. By balancing the rate of adsorption on the surface against the evaporation he obtained (12) an equation in the form

$$\frac{x}{m} = \frac{abp}{1 + ap}, \tag{1}$$

where x = weight of adsorbed material,

m = weight of adsorbent,

p = pressure of vapour,

and a and b are constants.

This equation gives an isotherm that is hyperbolic in form, rising rapidly at low pressures but becoming parallel to the pressure axis as ap becomes large compared with unity. The curve exhibits a saturation effect at high pressures, the adsorbed mass not increasing further with increase of pressure. This is to be expected according to this theory when the monomolecular layer becomes complete. Since the adsorption of water on cellulose shows no such saturation effect, this type of isotherm obviously will not satisfy the water–cellulose relation at high pressures, but it is instructive to compare the theoretical with the low pressure portion of the observational curve.

The curve marked I in Fig. 1 is obtained from Langmuir's equation in the form

$$\frac{x}{m} = \frac{52.85\, p/p_s}{1 + 4.95\, p/p_s}, \tag{2}$$

where p_s is the saturation pressure at the temperature in question. It is immediately evident that up to a relative humidity $p/p_s = 0.20$ this equation fits the experimental isotherm of Filby and Maass very nicely. This corresponds to an adsorption of about 0.05 gm. of water per gram of wood.

In their work Brunauer, Emmett, and Teller have assumed that at the point B, which is the point of inflection of the experimental curve, the adsorption ceases to be confined to a monomolecular layer and that there adsorption begins in the second and higher layers. On the simple Langmuir theory, B does not mark the point where the monomolecular layer is complete, since this would not occur until the Langmuir curve reached saturation and became parallel to the pressure axis, but rather indicates the point at which it is no longer possible to fit the experimental curve with a Langmuir equation. The fact that the experimental curve deviates from this theory at the point B indicates that adsorption takes place in the second layer long before the first layer becomes filled. This is to be expected when it is considered that the molecules will not be completely free to move over the surface and that there will be a Maxwell–Boltzmann distribution over the different sites. Above the point B then, the adsorption will take place concurrently in the first and second layers until the first layer is complete.

It is interesting, on the basis of this equation, to determine the extent of the adsorbed mass if the monomolecular layer were completed. This is obtained by substituting $p/p_s = 1.00$ in Equation (2). The value of $\frac{x}{m}$ obtained is 8.9%. Thus it appears from these considerations that 8.9 gm. of water is sufficient to cover completely the surface of 100 gm. of cellulose. This is considerably greater than the value found for B.

Recently Brunauer, Emmett, and Teller (5) have generalized Langmuir's adsorption isotherm to cover multimolecular adsorption. By applying Langmuir's assumptions to the second and higher layers they derived the following isotherm equation for multimolecular adsorption on a free surface.

$$\frac{p}{\frac{x}{m}(p_s - p)} = \frac{1}{\left(\frac{x}{m}\right)_s C} + \frac{C-1}{\left(\frac{x}{m}\right)_s C} \cdot \frac{p}{p_s}, \tag{3}$$

where $\frac{x}{m}$ is the weight adsorbed per unit mass of adsorbent at pressure p and absolute temperature T; p_s is the saturation vapour pressure; $\left(\frac{x}{m}\right)_s$ is the mass of gas adsorbed when the entire adsorbent surface is covered with a unimolecular layer; and C is approximately equal to $e^{\frac{E_1-E_L}{RT}}$, where E_1 is the heat of adsorption of the gas in the first adsorbed layer and E_L is the heat of condensation of the gas. If the function $\frac{p}{\frac{x}{m}(p_s-p)}$ is plotted against $\frac{p}{p_s}$ a straight line is obtained whose slope and intercept give the values of $\left(\frac{x}{m}\right)_s$ and C.

If the adsorption takes place in a limited space, so that, at saturation pressure, only a limited number of layers can be adsorbed on the adsorbent, there is obtained the expression

$$\cdot\ \frac{x}{m} = \frac{\left(\frac{x}{m}\right)_s Cy}{1-y} \cdot \frac{1-(n+1)\,y^n + ny^{n+1}}{1+(C-1)\,y - Cy^{n+1}}, \tag{4}$$

where $y = \frac{p}{p_s}$, $\left(\frac{x}{m}\right)_s$ and C have the same meaning as before, and n is the maximum number of layers of adsorbed gas that can build up on the walls of the capillaries, supposedly of plane parallel sides. Equation (4) reduces to Equation (3) when $n = \infty$, and in the other extreme case when only one adsorbed layer can form on the surface, i.e., when $n = 1$, it reduces to the Langmuir type equation,

$$\frac{p}{\frac{x}{m}} = \frac{p_s}{C\left(\frac{x}{m}\right)_s} + \frac{p}{\left(\frac{x}{m}\right)_s}. \tag{5}$$

Brunauer, Emmett, and Teller have suggested that a rather plausible interpretation of the constant n is that the width of the pores, cracks, and capillaries of the adsorbent sets a limit to the maximum number of layers that can be adsorbed even at saturation pressure. It is conceivable that factors other than the diameter of the capillaries can place a limit on the maximum number of layers that can be adsorbed, but Brunauer, Emmett, and Teller contend that Equation (4) should still remain valid.

In order to apply these equations to the experimental isotherm of Filby and Maass we shall start with Equation (3). To evaluate $\left(\frac{x}{m}\right)_s$ and C, $\frac{p}{x/m\,(p_s-p)}$ is plotted against p/p_s. This has been done in Fig. 2. The curve departs strongly from a straight line at high relative humidities, but up to 50% a linear relation is obtained. From the slope and intercept of the curve in Fig. 2 the following values are obtained for $\left(\frac{x}{m}\right)_s$ and C.

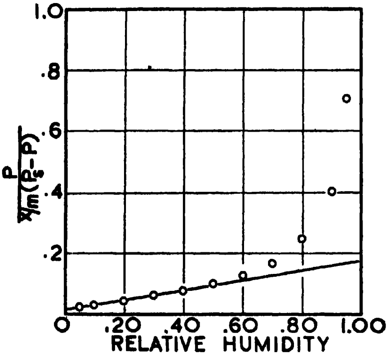


FIG. 2. *Plot of* $\frac{p}{x/m(p_s - p)}$ *against* p/p_s *for spruce wood.*

$$\left(\frac{x}{m}\right)_s = 6.17 \text{ and } C = 11.80.$$

On the basis of the fact that C is approximately equal to $e^{\frac{E_1-E_L}{RT}}$, the value of E_1-E_L can be obtained from the relation

$$E_1 - E_L = \frac{2.303\ RT \log_{10} 11.80}{18},$$

where E_1-E_L is the difference in the heat of adsorption in the first and subsequent layers per gram of water vapour. On this basis a figure of 80 cal. per gram is obtained. This result will be discussed further when the investigation of the heats of adsorption is described.

The values of $\frac{x}{m}$ obtained from Equation (3) by the use of these constants are shown in Fig. 1. These values deviate considerably from the experimental curve at high relative humidities as would be expected from Fig. 2. The rapid increase occurs at too low humidities although the similarity of the shape of the two curves indicates that some mechanism of this nature does take place in the vicinity of saturation.

The values obtained for $\left(\frac{x}{m}\right)_s$ and C can now be substituted in Equation (4). The results obtained from this equation for $n = 6$ and $n = 7$

are shown in Fig. 1. It is obvious that a value of n between 6 and 7 will give excellent agreement with the experimental curve up to relative humidities of 70% or more. Above this the experimental curve rises too steeply. There, capillary condensation undoubtedly occurs and it would be necessary to use some equation similar to Equation (3) but with the origin displaced.

At this point it is interesting to note that Equation (5) governing the Langmuir adsorption in the first layer, while being of the same form as Equation (2), does not have the same constants. It can be put in the form

$$\frac{x}{m} = \frac{C\left(\frac{x}{m}\right)_s p/p_s}{1 + C\, p/p_s}, \tag{6}$$

and substituting the values obtained for the constants C and $\left(\frac{x}{m}\right)_s$ the following expression is obtained.

$$\frac{x}{m} = \frac{72.9\, p/p_s}{1 + 11.80\, p/p_s}. \tag{7}$$

This curve coincides with the experimental data only for a small interval at low relative humidities; this indicates that the region in which the adsorbed molecules are confined to a monolayer is very small and that the adsorption in the second layer begins at a very early stage. It is interesting to note that the saturation value of Equation (6) is numerically very close to the point B in Fig. 1.

According to the above analysis the adsorption can conveniently be thought of as occurring in three distinct stages. First, at low humidities there is a small region where the adsorption may be considered as being monomolecular and where it proceeds according to Langmuir's mechanism. Secondly, there is in the second, third, and higher layers what may be called polymolecular adsorption and which can be treated in a manner similar to that adopted for monomolecular adsorption, but with the assumption that the energy involved is much smaller and is approaching that of the attraction of the free liquid. Finally, in the vicinity of saturation the adsorption proceeds by capillary attraction.

This hypothesis agrees with certain conclusions reached by Barkas (2, 3) from measurements on the shrinkage that occurs in wood exposed to different relative humidities and on changes in the strength of wood at different moisture contents. Barkas has distinguished between molecularly bound water and water retained by capillary adsorption. He concludes that until the moisture content is 6% all the water is molecularly bound. At 6%, capillary adsorption begins to occur but is not appreciable until the moisture content is about 16%, at which point his curves begin to deviate from the straight line corresponding to adsorption by molecular bonds only. If there were no capillary adsorption approximately 23 gm. would be adsorbed at saturation pressures. According to the theory of Brunauer, Emmett, and Teller the explanation of these facts is slightly different but is even more plausible. Their theory assumes that 6% is adsorbed in the first layer and up to 16% the adsorption is still molecular but occurs in the second and higher layers, while above 16% the adsorption is largely caused by capillary attraction.

The fact that this theory of polymolecular adsorption gives such a good explanation of these experimental facts provides substantial support for the assumption that the adsorption is not confined to a monomolecular layer. It is essential, therefore, at this stage to point out that a monomolecular theory is not thereby ruled out. In fact the essential point of the theory of Brunauer, Emmett, and Teller is that the force of attraction decreases after the first layer is filled. A similar effect might be obtained from monomolecular adsorption by assuming that a repulsion exists between the adsorbed molecules, so that, as the number of atoms in the monomolecular layer increases, the force attracting the molecules to the surface becomes less because of the mutual repulsion. Such a theory is very promising as it immediately gives a physical meaning to n, which then might be considered as the greatest number of near neighbours that any adsorbed atom might have. Such a force of repulsion between adsorbed atoms has in fact been found by Roberts (16); this will be discussed further when the heats of adsorption are considered.

Application to Cotton

It is also instructive to apply an analysis of this nature to cotton. For this purpose we use the data of Urquhart and Williams (22). In Fig. 3 the adsorption isotherm for soda-boiled cotton at a temperature of 20° C. has been reproduced. Again the hysteresis has been neglected as in the work on wood, and the study is confined to adsorption alone. In the same figure the points obtained by Filby and Maass for spruce wood are given, and the similarity in the shape of the two curves is immediately evident. However, the adsorption on the cotton is everywhere considerably less than that on the wood.

The equation of Brunauer, Emmett, and Teller will now be applied to this cotton isotherm. Proceeding in the same way as before and plotting $\frac{p}{x/m\ (p_s - p)}$ against p/p_s, we obtain the following values for C and $\left(\frac{x}{m}\right)_s$.

$$C = 16.07 \text{ and } \left(\frac{x}{m}\right)_s = 3.32\,.$$

Substituting these values into Equation (4) and solving for $n = \infty$ and $n = 6$, we obtain the two sets of values plotted in Fig. 3. It is evident that once again the curve with $n = 6$ gives excellent agreement up to relative humidities of 70%. It follows that the same considerations hold for cotton as were outlined above for wood. There is, however, some information to be obtained from the differences in the two cases.

In the first place, it is found here that the monomolecular layer is saturated when the moisture content is 3.32%. For wood this figure is 6.17%. The relative humidities corresponding to these two cases are 24.3% and 25.7%, respectively. It is evident that the vapour pressure at which the surface becomes saturated with a monomolecular layer is the same for cotton as for

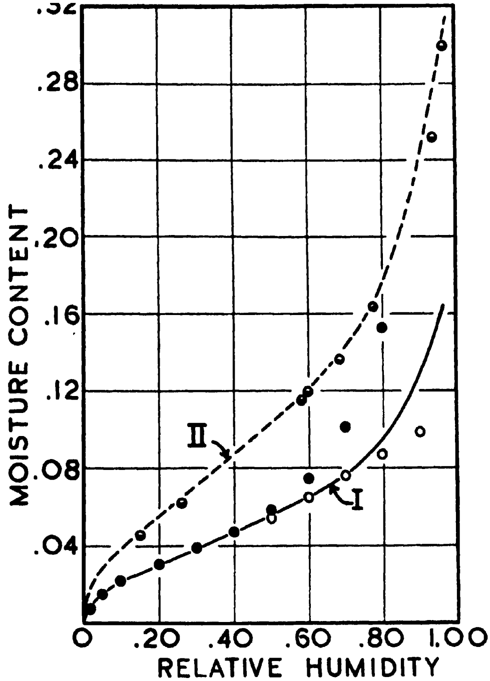


FIG. 3. *Comparison of isotherms for cotton and spruce wood. Full line, I, cotton (Urquhart and Williams). Broken line, II, = full line × 1.86. ⊖, Spruce wood, experimental data of Filby and Maass. Points ○ and ● are for n = 6 and n = ∞, respectively, in Brunauer's equation.*

wood. This indicates that the binding force between the water molecule and the cellulose is the same in the two cases. The fact that the cotton is saturated with a monomolecular layer with only 3.32% adsorbed, while wood requires 6.17%, indicates that the surface available in the case of cotton is only $\frac{3.32}{6.17} = 0.538$ that of the wood. This is interesting. It means that if the adsorptions obtained for cotton are multiplied by $\frac{1}{0.538} =$ 1.86 a curve would be obtained similar to that for wood. This has been done and the curve is virtually identical with the curve of Filby and Maass as shown in Fig. 3. There is one difficulty in this hypothesis, however. The value for C obtained on the basis of the theory of Brunauer, Emmett, and Teller is not the same for cotton and for wood. For spruce, the writer found $C = 11.80$ and for cotton it is equal to 16.07. Since C is approximately equal to $e^{\frac{E_1-E_L}{RT}}$ this indicates that E_1 cannot be the same in the two cases. Evaluating E_1-E_L for cotton we obtain

$$E_1 - E_L = \frac{2.303\ RT \log_{10} 16.07}{18}$$
$$= 89.5 \text{ cal.}$$

This figure of 89.5 cal. is to be compared with the figure of 80 cal. obtained for wood. This difference can be attributed at the present time only to experimental error, or to uncertainties in the theory.

This fact that the adsorption isotherms are identical except for a constant factor has important implications. In the first place it indicates that as far as adsorption of water is concerned, wood and cotton may be considered as identical except for the fact that the surface available for adsorption per gram of wood is 1.86 times that available per gram of cotton. In the second place it indicates that when equal fractions of the surface are covered in the two cases the equilibrium pressures are the same. From this it follows that the binding forces are identical.

The Heat of Adsorption

When gas is adsorbed on the surface of an adsorbent a quantity of heat is set free which is known as the heat of adsorption. This heat of adsorption is a measure of the energy that must be added to the adsorbed gas in order that it will have sufficient energy to break away from the attraction of the adsorbent. The heat of adsorption is thus an indication of the strength of the bond between the molecules of the adsorbed gas and the surface of the adsorbent. By studying the variation of the heat of adsorption with the quantity of gas adsorbed it should be possible to determine how the strength of bond between the adsorbed molecule and the underlying lattice is related to the adsorbed mass. In particular it might be expected that some indication would be found in the heat of adsorption if the adsorption changes from monomolecular to polymolecular. This point has been brought out in Brunauer, Emmett, and Teller's theory, and a value has already been obtained for the difference to be expected between the heat of adsorption and the latent heat of condensation. It is interesting therefore to examine all the data available in order to ascertain how their assumptions are supported.

The information available on the heats of adsorption of cellulose is not extensive, and in order to obtain a complete picture it is necessary to piece together data from different sources. The direct measurements are confined to some on the integral heat of adsorption of cellulose by Katz (11), similar measurements on prepared wood fibre by Volbehr, which are also quoted by Katz (11), and a series of determinations by Argue and Maass (1) on the heat of wetting of cellulose by water. Fortunately it is possible, by the use of the Clausius–Clapeyron equation, to calculate the heats of adsorption from vapour-pressure–adsorption equilibrium data. If two adsorption isotherms are obtained at temperatures not too far apart the heat of adsorptions can be quite easily determined. There is no reason to believe that this method does not give accurate and true results, and it has been used extensively in the calculation of the heat of adsorption for other materials. Stamm and Loughborough (20) have applied this method to a mass of data that they have obtained for the equilibrium of Sitka spruce and water vapour and these data are available for this study. There are also some results of Pidgeon and Maass (15) on the adsorption by spruce wood that can be used for this purpose. However, by far the most complete series of results is given by Urquhart and Williams (22) for cotton, and their work will be used as the main basis for our calculations.

It is obvious from what has been said in the foregoing section that the binding force between adsorbate and adsorbent should depend on the fraction of available surface covered and, as was shown, this is a function of the equilibrium pressure; for the same pressure the heats of adsorption of wood and cotton should be the same. In the work that follows the relation between heat of adsorption and relative vapour pressure will be considered.

In all the direct measurements of the heats of adsorption the quantity measured is the heat of wetting, that is, the heat that is given off when the adsorbent is brought into contact with liquid water. It is assumed that this heat of wetting is equal to the net heat of adsorption, defined by the relation

$$\lambda_n = \lambda_t - L,$$

where λ_t is the total heat given off when water in the vapour phase is adsorbed and L is the latent heat of evaporation. The experiments give the integral heats of adsorption, and the differential heats, in which we are interested, can be obtained from these by differentiation.

Katz in his work found that the curve relating the integral heat of adsorption with the amount adsorbed could be expressed by an equation of the form

$$W = \frac{A\frac{x}{m}}{B + \frac{x}{m}},$$

where W is the integral heat of adsorption and A and B are constants. He found that for cellulose and prepared wood fibre these constants had the following values.

	A	B
Cellulose	11.6	0.030
Prepared wood fibre	23.62	0.0895

The differential heat of adsorption can be obtained from these equations by differentiation. Thus,

$$\lambda_n = \frac{dW}{d\left(\frac{x}{m}\right)} = \frac{AB}{\left(B + \frac{x}{m}\right)^2}.$$

In Tables I and II below, the values obtained from this equation for λ_n in the case of cellulose and prepared wood fibre respectively are given.

The values for $\frac{x}{m}$ given in Tables I and II have been derived from the relative humidity by means of Figs. 3 and 1 respectively. Katz does give an isotherm for cellulose from which it would have been possible to determine the relation between $\frac{x}{m}$ and the relative humidity, but it was found after trial that there was little difference in the curves, and the values of Urquhart

TABLE I

DIFFERENTIAL HEAT OF ADSORPTION FOR CELLULOSE TAKEN FROM DATA OF J. R. KATZ

Relative humidity, %	$\frac{x}{m}$	$\lambda_n = \frac{0.348}{(0.030 + \frac{x}{m})^2}$, cal.
0.0	0.000	387
2.0	0.009	232
5.0	0.015	174
10.0	0.022	129
20.0	0.030	98
30.0	0.039	74
40.0	0.047	58
50.0	0.055	48
60.0	0.065	38
70.0	0.077	30
80.0	0.095	22
90.0	0.128	14

TABLE II

DIFFERENTIAL HEAT OF ADSORPTION FOR PREPARED WOOD FIBRE TAKEN FROM DATA OF J. R. KATZ

Relative humidity, %	$\frac{x}{m}$	$\lambda_n = \frac{2.114}{(0.0895 + \frac{x}{m})^2}$, cal.
0.0	0.000	264
2.0	0.009	216
5.0	0.021	173
10.0	0.035	135
20.0	0.054	103
30.0	0.068	85
40.0	0.084	71
50.0	0.100	59
60.0	0.120	48
70.0	0.141	40
80.0	0.173	31
90.0	0.225	21

and Williams gave a slightly smoother relation between relative humidity and heat of adsorption. The results in Tables I and II have been plotted in Fig. 4.

Argue and Maass in their work (1) give directly the total heat of adsorption of water vapour adsorbed on a cellulose prepared from pure cotton. The experimental method was similar to that used by Katz but they have handled their results in a slightly different manner. The results have been reproduced in Table III. The values of the relative humidity given in the second column of Table III were obtained from the adsorption curve of Urquhart and Williams, which is reproduced in Fig. 3. There is a possibility that the cellulose used by Argue and Maass would have an adsorption isotherm differing slightly from this curve, but since they do not give adsorption data for their cotton the curve of Urquhart and Williams is used. The data from Table III have been plotted in Fig. 4.

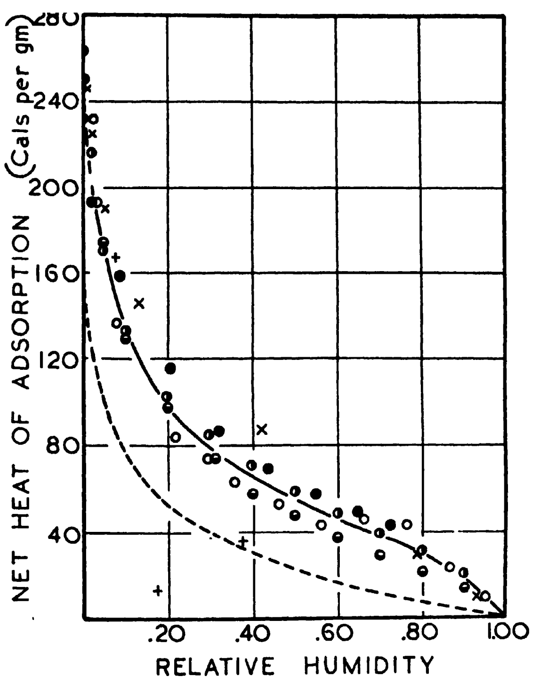


FIG. 4. *Heats of adsorption.* ● *Cotton (Argue and Maass).* ×, *Spruce wood (Stamm and Loughborough).* +, *Spruce wood (Pidgeon and Maass).* ○, *Cotton (Urquhart and Williams).* ⊖, *Cellulose (Katz)* ◑, *Prepared wood fibre (Katz).* ------, *Free energy,* $\frac{RT}{M}\log_e\frac{p_s}{p}$.

TABLE III

DIFFERENTIAL HEATS OF ADSORPTION FOR COTTON CELLULOSE AT 25° C., TAKEN FROM DATA OF ARGUE AND MAASS

Moisture content, %	Relative humidity, %	λ_t, cal.	λ_n, cal.
0.00	0.0	832.0	250.0
0.005	1.0	814.0	232.0
0.01	2.4	775.0	193.0
0.02	8.9	740.0	158.0
0.03	20.9	697.9	115.9
0.04	32.0	668.9	86.9
0.05	43.7	651.6	69.6
0.06	55.0	639.9	57.9
0.07	64.7	631.7	49.7
0.08	72.3	625.5	43.5

As mentioned above, it is possible to calculate the heats of adsorption from adsorption data by use of the Clausius–Clapeyron equation. This equation can be written in the form

$$\lambda_t = \frac{RT^2}{Mp}\frac{dp}{dT}, \tag{8}$$

where R is the gas constant (1.98 cal./° C.),
M, the molecular weight of the vapour,
and p, the equilibrium pressure.

Equation (8) is equivalent to

$$\lambda_t = \frac{RT^2}{M}\frac{d(\log_e p)}{dT}, \tag{9}$$

so that if $\frac{d(\log_e p)}{dT}$ can be evaluated it is a simple matter to calculate λ_t. Since the majority of workers in reporting adsorption data give isosteres where log p is plotted against $\frac{1}{T}$ in addition to the isotherms, there is no difficulty in using Equation (9).

The first data to which this procedure will be applied are those of Stamm and Loughborough (20). The graphs given by them in their paper unfortunately proved to be too small to enable reliable results to be obtained but Dr. A. J. Stamm has kindly calculated the heats of adsorption for us from the original data in his possession. The values of λ_n for different moisture contents and corresponding relative humidities as calculated by Dr. Stamm are given in Table IV. The data from this table have been plotted in Fig. 4.

TABLE IV

DIFFERENTIAL HEAT OF ADSORPTION CALCULATED FROM DATA OF STAMM AND LOUGHBOROUGH FOR SITKA SPRUCE WOOD AT A TEMPERATURE OF 20.0° C.

Moisture content, %	Relative humidity, %	λ_n, cal.
0.5	1	246
1.0	2	225
2.0	5	190
4.0	13	146
8.0	42	88
16.0	79	30
24.0	93	10

It is also possible to calculate the heat of adsorption of spruce wood from some data given by Pidgeon and Maass (15). They measured the adsorption equilibrium at several different temperatures and have calculated adsorption isosteres, so that it is possible to apply the same procedure to their results as has been used above in the case of Stamm and Loughborough. It is true that these measurements of Pidgeon and Maass have been found by both Urquhart and Williams and Filby and Maass to be too low at high humidities, but since their results below 70% relative humidity agree substantially with those of Filby and Maass it should be allowable to use them for our purpose.

In order to obtain a value for $\frac{d\,(\log_e p)}{dT}$, tangents were drawn to the isosteres given in Fig. 7 of Pidgeon and Maass's paper. The values were taken at 20° C. and are given in the table below, together with the heats of adsorption derived from them.

TABLE V

HEATS OF ADSORPTION FOR SPRUCE WOOD AT 20° C. CALCULATED FROM DATA OF PIDGEON AND MAASS

Moisture content, %	p/p_s, %	λ_t, cal.	λ_n, cal.
1	2.1	1276.0	691.1
2	4.8	1190.0	605.1
3	8.0	751.0	166.1
5	17.8	598.0	13.1
8	37.8	620.4	35.5

The values obtained here for the 3, 5, and 8% moisture content are roughly equivalent to the values obtained from the data of Stamm and Loughborough. The values at 1 and 2% are much larger. A glance at the isosteres given by Pidgeon and Maass is sufficient to explain this, as the points used in plotting the isosteres are so scattered that it is almost impossible to obtain an accurate estimate of the tangent. There is also some doubt with regard to the 3, 5, and 8% curves, but at least these can be considered to be approximately correct. They have been plotted in Fig. 4.

Finally, the data of Urquhart and Williams (22) can be used to calculate the heats of adsorption for soda-boiled cotton. Since they give log p plotted against $\frac{1}{T}$ in their Fig. 4 it is possible to apply the Clausius-Clapeyron equation as given in Equation (9) directly to their work. The values obtained in this way for a temperature of 20° C. are given in Table VI.

The figures in Table VI have been plotted in Fig. 4 along with the rest of the heats of adsorption. It is to be seen from this figure that the data from the different sources agree fairly well with the exception of a few isolated points, and it may be assumed that this disagreement is the result of experimental error. It is especially interesting to note that when the heats of adsorption are plotted in this way there does not appear to be any significant difference between those obtained from cotton and those obtained from wood. This supports our hypothesis that the adsorption in these two cases is similar and differs only in the area of surface available for adsorption. A mean curve has been drawn through the points in Fig. 4, and this may be taken as representing the variation of the heat of adsorption with relative humidity.

TABLE VI

DIFFERENTIAL HEATS OF ADSORPTION OF SODA-BOILED COTTON AT 20° C., FROM THE DATA OF URQUHART AND WILLIAMS

Moisture content, %	Relative humidity, %	λ_t, cal.	λ_n, cal.
1.2	3.2	778	193
1.9	8.0	722	137
3.1	22.0	669	84
3.8	29.8	659	74
4.3	35.8	648	63
5.2	46.0	638	53
6.1	56.0	628	43
7.2	66.3	631	46
8.7	76.5	628	43
11.5	86.8	608	23
15.7	95.0	595	10
19.9	98.7	590	5

It is to be noted that this curve gives an initial heat of adsorption at zero vapour pressure of approximately 280 cal. This is in excellent agreement with the value of 289 cal. given by Neale and Stringfellow (13), who have investigated the adsorption of water vapour by cotton at very low relative humidities.

The curve in Fig. 4 exhibits the same general tendencies as a curve given by Williams (23) for the heats of adsorption obtained when sulphur dioxide is adsorbed by charcoal. Both curves fall rapidly with increasing relative humidities at low humidity, flatten out in the middle humidity region, and then fall more rapidly to zero as saturation is approached. Since the isotherm for the adsorption of sulphur dioxide on charcoal also has a sigmoid shape it may be that all heats of adsorption pertaining to this type of isotherm are of a similar nature. It is, however, interesting to note that Williams' curve shows a definite maximum before the final fall to zero and also there seems to be an indication that in his case the heat of adsorption becomes zero before saturation pressures are reached.

The Thermodynamics of Adsorption

It is obvious that the adsorption of a vapour is a phenomenon that is closely related to condensation. We have assumed this in the discussion of the experimental work on the heats of adsorption and have defined the net heat of adsorption as the total heat minus the latent heat of condensation. It is therefore instructive to follow up this idea and to determine as closely as possible the relation that exists between the heat of adsorption and the heat of condensation. Many workers have expressed such relations but since it is difficult to find an explicit derivation, this matter will be considered in some detail.

In its thermodynamical aspects, adsorption is very similar to solution, and a great deal of the theory of dilute solutions can be applied to adsorption.

This forms the basis of the work given below, in which the relation between heat of adsorption and heat of condensation is shown.

Let us first of all consider a mass of adsorbing material of sufficient size so that the removal of unit mass of adsorbate will not noticeably affect the adsorption ratio. It is assumed that the adsorbed mass is $\frac{x}{m}$ grams per gram of adsorbent and that the equilibrium vapour pressure of the adsorbate is p. It will be considered also that the external hydrostatic pressure on the adsorbent is p, that is to say, the system is under its own vapour pressure. On the other hand, we shall consider a quantity of the liquid adsorbate also under its own pressure, which in this case is equal to p_s, the saturation vapour pressure at the temperature T.

We wish to bring the adsorbing system into equilibrium with the liquid adsorbate and in order to accomplish this we shall increase the external hydrostatic pressure on the adsorbent to a value $P + p$ such that the vapour pressure over the adsorbent becomes equal to p_s. (The value of $P + p$ can be determined from the equation,

$$\frac{dp}{dP} = \frac{s}{v},$$

where s is the volume occupied by the adsorbate in the adsorbed state and v the volume in the vapour state. See, for instance, O. Sackur: "Thermochemistry and Thermodynamics": Trans. by G. E. Gibson, pp. 219-220. 1917.) P may be considered as the swelling pressure and is similar to the osmotic pressure of solutions.

The adsorbent and the liquid adsorbate can now be brought into contact by the arrangement shown in Fig. 5. The adsorbent is separated from the liquid adsorbate by a semipermeable membrane C that is permeable to the adsorbate but not to the adsorbent. The adsorbent is confined by a piston A on which the pressure is $P + p$, and the adsorbate by a piston B on which the pressure is p_s. A lateral cylinder leads off from each chamber and is separated from the chambers by diaphragms permeable to the vapour alone. The pressures in these lateral cylinders are maintained at p_s by the pistons D and E. The whole system is thus in equilibrium and we may consider the following cycle in which all the steps are reversible.

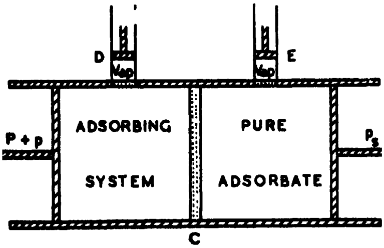


FIG. 5

(1) Unit mass is evaporated from the liquid adsorbate and removed by means of the lateral cylinder. The pressure is maintained at p_s by piston *B*. The heat added to the system during this step is equal to *L*, the latent heat of evaporation under pressure p_s.

(2) The unit mass of vapour is transferred to the adsorbent by means of the second lateral cylinder, and there it is adsorbed. The heat involved in this process is λ_{P+p}, which is the heat of adsorption at pressure $P + p$.

(3) Unit mass of adsorbate is transferred from adsorbent to the liquid adsorbate through the semipermeable membrane *C* by movement of the pistons. The work done

$$dw = -\int_{P+p}^{p_s} s\,dp,$$

where s is the volume occupied by unit mass of the adsorbate. Now we have $\frac{ds}{dp} = \kappa$, the compressibility of the adsorbate, and we may assume that κ is a constant. Hence $s = \kappa p$.

Thus
$$dw = -\int_{P+p}^{p_s} \kappa\,p\,dp$$
$$= -\frac{\kappa}{2}\left[p_s^2 - (P+p)^2\right],$$

and since p_s and p are small compared with P

$$dw = \frac{\kappa}{2}P^2 .$$

Besides this work that is performed in transferring the adsorbate from the adsorbent to the liquid, it is necessary to recognize the possibility that there may be a change of state in passing from the adsorbed phase to the liquid phase. It is probable that there is a greater degree of organization in the adsorbed phase than in the liquid corresponding to a certain amount of solidification, so that it may be necessary to add an energy term corresponding to a change of state. This can be best done by assuming an increase in entropy equal to ΔS in passing to the liquid state, so that the energy change is $T\Delta S$.

The system is now back in its original state and since the cycle was carried out at constant temperature the sum of the energy changes involved must equal zero. Hence

$$L - \lambda_{P+p} + \frac{\kappa}{2}P^2 + T\Delta S = 0. \qquad (10)$$

Under ordinary conditions an adsorbent is either under atmospheric pressure or the equilibrium vapour pressure, so that now the relation between λ_{P+p} and λ_p must be found.

In order to do this consider a quantity of adsorbent confined in a chamber fitted with a piston and a lateral cylinder as shown in Fig. 6. Here again the membrane separating the chamber from the lateral cylinder is permeable to the vapour only.

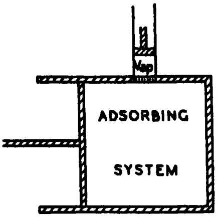


FIG. 6

We now consider the following reversible steps:

1. Unit mass of adsorbate is evaporated from the adsorbent and removed through the lateral chamber, the pressure being maintained at p by means of the piston. The heat added to the system is λ_p.
2. The vapour is compressed from pressure p to saturation pressure p_s.

$$\text{Work done} = -\int_p^{p_s} v\,dp$$

$$= -\int_p^{p_s} \frac{RT}{M}\,\frac{dp}{p}$$

$$= -\frac{RT}{M}\log_e\frac{p_s}{p}.$$

3. The adsorbing system in the chamber is compressed to a pressure $P + p$ by means of the piston.

$$\text{Work done} = -\int_p^{P+p} (V - s)\,dp,$$

where V is the original volume of adsorbent plus adsorbate and s is the volume decrease resulting from the removal of unit mass of adsorbate.

4. The vapour is adsorbed on the adsorbent by means of the lateral cylinder. Heat given out $= -\lambda_{P+p}$.
5. The adsorbent plus adsorbate is expanded to original pressure p.

$$\text{Work done} = -\int_{P+p}^{p} V\,dp$$

The system is now in its original state so that the sum of the energies must equal zero. Thus

$$\lambda_p - \frac{RT}{M}\log_e\frac{p_s}{p} - \int_p^{P+p}(V-s)\,dp - \lambda_{P+p} - \int_{P+p}^{p} V\,dp = 0,$$

which becomes $\lambda_p - \dfrac{RT}{M}\log_e\dfrac{p_s}{p} + \displaystyle\int_p^{P+p} s\,dp - \lambda_{P+p} = 0.$

But now we have, as before, $s = \kappa p$, so that

$$\int_p^{P+p} s\,dp = \frac{\kappa}{2}\left[(P+p)^2 - p^2\right] = \frac{\kappa}{2}P^2.$$

Thus
$$\lambda_{P+p} = \lambda_p - \frac{RT}{M}\log_e\frac{p_s}{p} + \frac{\kappa}{2}P^2.$$

Substituting this into the expression for λ_{P+p}, we find

$$L - \lambda_p + \frac{RT}{M}\log_e\frac{p_s}{p} + T\Delta S = 0$$

or

$$\lambda_p = L + \frac{RT}{M}\log_e\frac{p_s}{p} + T\Delta S. \qquad (11)$$

Remembering the definition of the net heat of adsorption λ_n, we find

$$\lambda_n = \frac{RT}{M}\log_e\frac{p_s}{p} + T\Delta S. \qquad (12)$$

Now $\frac{RT}{M}\log_e\frac{p_s}{p}$ is simply the free energy of expansion of a gas from the pressure p_s to the pressure p. We shall calculate this for water vapour and compare the values obtained with those of λ_n given in Fig. 4. The difference between λ_n and the free energy will be equal to $T\,\Delta S$, which can be considered as the change in internal energy of the water vapour during the transition from the adsorbed to the free state. The value of $\frac{RT}{M}\log_e\frac{p_s}{p}$ for different relative humidities is given in Table VII, and these values have been plotted as the broken curve in Fig. 4.

It is interesting to note that when the free energy is considered as a function of the relative humidity, the resulting curve is independent of the nature of the adsorbent. It is only when the relation between free energy and moisture

TABLE VII

VALUE OF $\frac{RT}{M}\log_e\frac{p_s}{p}$ FOR 20° C.

Relative humidity, %	$\frac{RT}{M}\log_e\frac{p_s}{p}$, cal.	Relative humidity, %	$\frac{RT}{M}\log_e\frac{p_s}{p}$, cal.
0.1	222.6	40.0	29.9
0.5	170.8	45.0	26.1
1.0	148.4	50.0	22.6
2.0	126.1	55.0	19.6
4.0	103.8	60.0	16.8
5.0	96.8	65.0	14.1
10.0	75.3	70.0	11.7
15.0	62.0	75.0	9.3
20.0	52.6	80.0	7.3
25.0	45.3	85.0	5.4
30.0	39.3	90.0	3.4
35.0	34.3	95.0	1.6

content is considered that the nature of the adsorbent becomes important. This stresses once again the convenience of using the relative humidity as the independent variable rather than the moisture content.

Fig. 4 shows immediately that there is definitely a change of phase in passing from the adsorbed state to the liquid state. The experimental points for the heats of adsorption are nearly all well above the free energy curve and the difference between them and the curve is, at all relative humidities; quite appreciable. This difference has been calculated. It is shown in Table VIII and the resulting curve is given in Fig. 7.

TABLE VIII

Moisture content (cotton), %	Relative humidity, %	λ_n	$\frac{RT}{M}\log_e\frac{p_s}{p}$	$T\Delta S = \lambda_n - \frac{RT}{M}\log_e\frac{p_s}{p}$
0.5	1.0	230.0	148.4	81.6
0.9	2.0	210.0	126.1	83.9
1.5	5.0	173.0	96.8	76.2
2.1	10.0	136.0	75.3	60.7
2.5	15.0	113.5	62.0	51.0
2.95	20.0	98.5	52.6	45.9
3.4	25.0	87.8	45.3	42.5
3.8	30.0	79.2	39.3	39.9
4.3	35.0	72.1	34.3	37.8
4.7	40.0	66.0	29.9	36.1
5.1	45.0	60.0	26.1	33.9
5.6	50.0	54.7	22.6	32.1
6.0	55.0	49.9	19.6	30.3
6.6	60.0	45.2	16.8	28.4
7.0	65.0	41.0	14.1	26.9
7.7	70.0	37.8	11.7	26.1
8.4	75.0	34.3	9.3	25.0
9.5	80.0	29.5	7.3	22.2
10.9	85.0	24.0	5.4	18.6
12.8	90.0	17.5	3.4	14.1
15.6	95.0	10.0	1.6	8.4

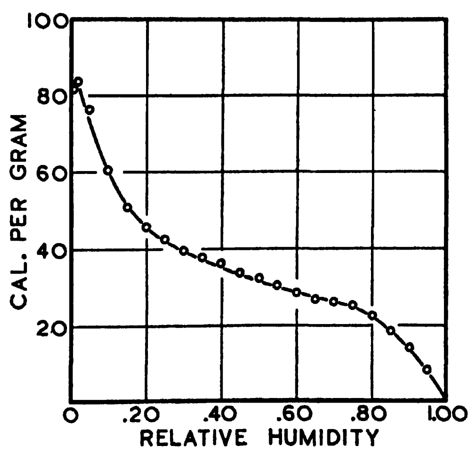


FIG. 7. *Excess of net heat of adsorption over free energy.*

There is one interesting point to consider in connection with the free energy. According to the expression $\frac{RT}{M} \log_e \frac{p_s}{p}$ the free energy should be infinite when the equilibrium pressure p approaches zero, and consequently the heat of adsorption should also become infinite. This does not seem to be borne out by any of the experimental work. In particular the experiments of Neale and Stringfellow (13), which were carried out at moisture contents as low as 0.00012 gm. per gm. of adsorbent indicate that there is no appreciable change in the heat of adsorption when the moisture content varies from 0.001 to 0.00012 gm. per gm. of adsorbent. The lowest of these moisture contents corresponds to a relative humidity of 0.006% and at this point the free energy would be 313 cal. per gram. Since Neale and Stringfellow found the net heat of adsorption to be only 289 cal. it appears that our relation derived above cannot hold in this region unless the experimental work is in error; this seems very unlikely. However, there is no reason to doubt the validity of our results at higher pressures and we shall consider that Fig. 7 gives a measure of the difference in internal energy between adsorbed moisture and liquid water until very low relative humidities are reached.

Fig. 7 then may be considered as indicating the state of the water vapour adsorbed on the cellulose surface. It shows by how much the energy of binding of the water molecule to the cellulose crystal is greater than the force of attraction between a water molecule and a free water surface. The first point of interest is to note that the molecule is more strongly attracted at low vapour pressures. The first atoms are either adsorbed on sites on the surface where the attractive force is greater than on the rest of the surface or the adsorbed atoms exert a repulsive force on one another so that as more atoms are adsorbed the attracting forces become smaller. This is explained on Brunauer, Emmett, and Teller's theory by assuming that as the number of adsorbed layers increase, the attracting force becomes less. However, according to this theory, a number of steps might be expected rather than a smooth curve. In particular there should be a break in the curve at the point where the adsorption changed from monomolecular to polymolecular adsorption. This transition occurs at approximately 20% relative humidity as shown in Fig. 1 and there is no sign of a break in Fig. 7 at this point. However, it must be remembered that according to this theory the condensation does not change sharply, but there is an overlapping, so that condensation begins in the second layer long before the first layer is completed. In this manner a smooth curve similar to that found in Fig. 7 might be obtained.

Another interesting point about Fig. 7 is the tendency for the curve to flatten out at relative humidities around 60 to 70%; only above that point does it start to fall to zero at saturation. The rapid drop between 80 and 100% relative humidity can be assumed to be caused by the change to capillary adsorption that takes place in that region and corresponds to the steep portion of the isotherm. The flat portion of the curve apparently indicates that were capillary adsorption not present there would be an energy difference between adsorbed and free moisture even at saturation. As long as adsorption is molecular rather than capillary it can be assumed that there is an entropy difference between the adsorbed and liquid states.

It is difficult to account for a residual energy of this nature on the polymolecular theory since according to this theory the heat of adsorption was assumed to approach the latent heat of condensation as the number of layers increased. On the basis of a monomolecular theory, however, such a residual energy would represent the energy of attraction of the surface minus the repulsive forces of the neighbouring adsorbed atoms.

It is interesting to note that the water initially adsorbed at low humidities has an excess energy of between 80 and 90 cal. This is in good agreement with the values obtained by evaluating $E_1 - E_L$ in the theory of Brunauer, Emmett, and Teller.

With respect to the heat of adsorption curve it is interesting to examine the explanation that Roberts (16) suggests for the curve found by Williams for the adsorption of sulphur dioxide on charcoal. As mentioned previously this curve is very similar in shape to that obtained for adsorption of water on cellulose. Roberts assumes that the adsorption is monomolecular and that the shape of the heat of adsorption curve can be attributed to the fact that the interaction between adsorbed molecules arises partly from van der Waals' attractive forces and partly from repulsions between permanent or induced dipoles. On page 101 of his book, Roberts gives curves showing how these two types of forces would vary with the fraction of surface covered, and by adding the two effects he obtains a curve that has the general features of the sulphur dioxide adsorption curve of Williams. Roberts assumes that the initial rapid drop found with such heat of adsorption curves "is presumably due to adsorption in crevices where an adsorbed atom is influenced by an abnormally high number of atoms of the solid."

The Problem of the Adsorption Compression

It is an established experimental fact that when water is adsorbed on cellulose the final volume is less than the sum of the original volumes of the cellulose and the water (8, 9, 11, 19, 21). There is a contraction in the total volume similar to that found in the case of certain aqueous solutions. It is generally assumed that this volume contraction is confined to the water and that there is no variation in the size of the cellulose crystals. (There is evidence for this assumption in the fact that there is no change in the X-ray diagrams of cellulose when water is adsorbed.) It is also assumed that the decrease in the size of the water molecules is due to the compression caused by the strong adsorptive forces of the cellulose. Any theory of adsorption must account for this adsorption compression. If it is the result of the strong attractive forces then it must be assumed either that (i) the length of the bond between the water and cellulose is less than that of the bond between water and water, or (ii) the water molecules are packed more closely on the surface of the cellulose than they are in the natural state. It will be shown that the second of these hypotheses seems to offer an adequate explanation and gives a satisfactory picture of the phenomenon.

When the specific volume of cotton cellulose is determined by density measurements in helium, a value of 0.642 cc. is obtained, while similar measurements in water yield a value of 0.621 cc. (8, 9). There is thus a difference of 0.021 cc. in the apparent specific volume in the two cases. Similar measurements for white spruce wood substance given by Stamm (18) are 0.685 and 0.654 in helium and water, respectively. This represents a contraction of 0.031 cc. These facts are explained by assuming that helium is negligibly adsorbed so that the helium value represents the true volume of the cellulose and the smaller volume obtained with water is the result of the fact that adsorbed water does not occupy its ordinary volume.

Measurements are available giving this contraction in volume as a function of the moisture content of the cellulose. Thus J. R. Katz (11) gives the volume contraction when 1 gm. of wood fibre adsorbs $\frac{x}{m}$ grams of water. (His results are the mean values taken from measurements of H. Volbehr.) Filby and Maass (9) have calculated the apparent density of water adsorbed on cotton cellulose as a function of the adsorbed mass, and A. J. Stamm (18) has made similar calculations for white spruce wood substance. In order to compare these results we shall put them all in the form given by Katz, i.e., the total volume contraction when 1 gm. of dry adsorbent adsorbs $\frac{x}{m}$ grams of water. The results of Filby and Maass can be put in this form by plotting the specific volume of the water adsorbed at the different moisture contents and integrating graphically. The volume contraction can then be easily obtained by subtracting the resulting values from the volume that the water would occupy if the density had been unity. Stamm gives his results as the average density of adsorbed water at each moisture content. It is possible therefore to determine the average specific volume of the water at the different moisture contents and by subtraction to obtain the average contraction in volume. Multiplying this contraction by the corresponding moisture content gives the integral contraction at that moisture content. The results from the measurements are reproduced in Fig. 8.

It is to be noticed that there is fair agreement between the results of Filby and Maass and those of Katz, but that Stamm's measurements are considerably less. This might be caused by the difference in the materials used, as it is hardly to be expected that the spruce wood used by Stamm would give the same results as the cotton cellulose used by Filby and Maass or the "veränderte holzfaser" used by Katz. It is, however, surprising that Katz's measurements agree with those of Filby and Maass rather than with Stamm's.

There is one further point to be observed in connection with the measurements. Filby and Maass, and Katz, find the total contraction when the substance is saturated to be 0.045 cc., while Stamm finds it to be about 0.31 cc.

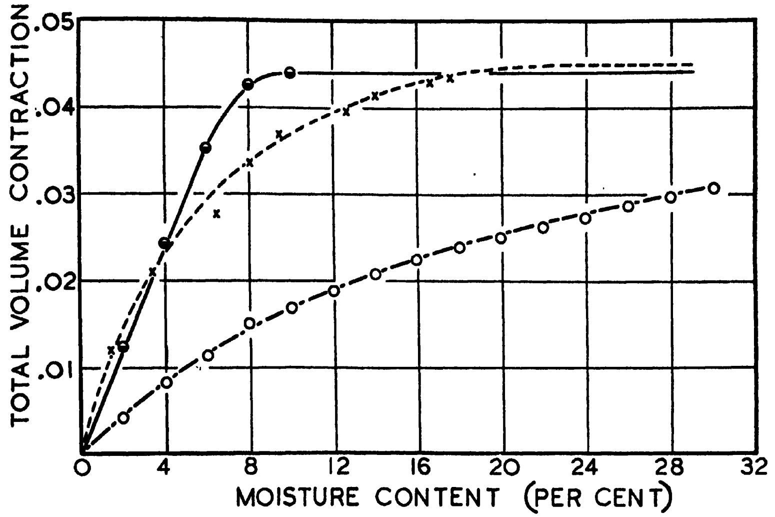


FIG. 8. *Total volume contraction in cubic centimetres per gram of adsorbent.* ⊖, *Filby and Maass.* X, *Katz.* O, *Stamm.*

This contraction should check with the differences in the specific volumes found by measurements in helium and water. As mentioned previously the contraction found in that way was 0.021 cc. for cotton and 0.031 cc. for white spruce wood. Stamm's value does agree with the latter but since he used this value originally in calculating his densities no added significance can be obtained from the coincidence. The value of 0.045 cc. however does not agree with either the results from cotton or those from spruce wood. This is sufficient to cause considerable doubt regarding the accuracy of these measurements and indicates the need for more work of this nature.

The values that Filby and Maass obtain for the densities of the water originally adsorbed by the cellulose are very interesting if reliance can be placed in them. Below 3% moisture content they find a uniform density of 2.6 gm. per cc. At higher moisture contents the apparent density becomes less, until above 9% moisture content the water adsorbed appears to have its normal density.

These figures are surprising. A density of 2.6 represents a specific volume of 0.38 cc., and to compress water to this extent by means of an externally applied force would require a pressure of several hundred thousand atmospheres. If the bond between the cellulose and the water is so much stronger than the bond in liquid water a heat of adsorption of a completely different order of magnitude from that of the latent heat of evaporation should be expected. It should rather approximate to the heat of formation of a water molecule from hydrogen and oxygen.

The work of Stamm and Seborg (21) has thrown considerable doubt on these measurements of Filby and Maass. They find that contrary to the latter's results the compression does not become zero for moisture contents above 9% but continues to the fibre-saturation point. They also find (18) that the density of the water originally adsorbed is 1.30, representing a specific volume of 0.77 cc. This is considerably different from the specific volume of 0.38 cc. found by Filby and Maass, and it is quite easy to conceive that water is compressed to this extent by the application of an external pressure.

There is also reason to believe that the data of Katz give too great a compression. Katz calculated the volume contraction for different amounts of adsorbed water on the basis that the void structure of wood fibre was completely filled by petroleum ether. Stamm and Seborg (21) have shown that this is not the case and that the true specific volume is lower than that determined from such measurements. It is probable, that, for this reason, Katz's results given in Fig. 8 are high.

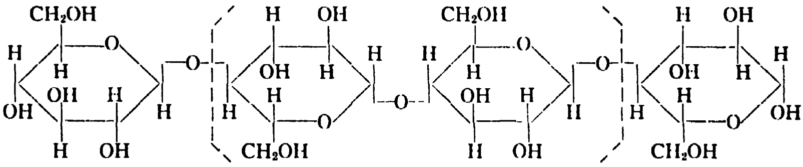
It would seem, therefore, that the data of Stamm give the most reliable estimate of the amount of the volume contraction. We must now endeavour to find a reasonable explanation of how such a compression can occur.

According to the picture of water put forward by Bernal and Fowler (4) the water molecules in ice are arranged in a somewhat distorted tetrahedral system. Each oxygen atom is connected with four other oxygen atoms and the hydrogen atoms lie on the lines joining the oxygen atoms, but are not midway between them. Each oxygen atom has two hydrogen atoms at a distance of 0.99Å, corresponding to the gaseous molecule where the distance is 0.96 Å, and two other hydrogen atoms at a distance of 1.77 Å. Thus the distance between the oxygen atoms is 2.76 Å. Bernal and Fowler found that this structure also prevails to a certain extent in liquid water, but in this case at room temperatures it is continually alternating with a quartz type of structure. This conception of water represents a very open structure, for were the water molecules having a diameter of 2.76 Å arranged in the most compact configuration possible a structure would be obtained with a density of about 1.8, i.e., it would be nearly twice as dense as water.

Thus there is much open space in liquid water and by a rearrangement of the molecules it would be easily possible to account for a density of 1.30. In fact, a density of this order has been found for certain types of ice. Bernal and Fowler, quoting from the data of Bridgman, show that ice VI, which exists at pressures above 6000 atm., has a specific volume of 0.76 cc. This corresponds very closely to the density observed by Stamm for the water initially adsorbed on cellulose. There would be then no difficulty from molecular considerations in accounting for the decreased volume of this adsorbed water. It must be remembered, however, that at low moisture contents the number of molecules is so small that the monomolecular layer is far from complete and any comparison with the structure of ice may be misleading. The problem is rather to attach the water molecules to the surface of the cellulose in such a way that they will occupy less volume than they would if attached to a free water surface, and at the same time to account for the excess energy of binding. We shall consider how this might occur.

The oxygen molecules in water are united by a hydrogen bond. According to Pauling the strength of the bond O-H-O in water is 4.5 kcal. per mole and the distance between the oxygen molecules is 2.76 Å. In vaporizing ice it is necessary to break two hydrogen bonds per molecule. The latent heat of vaporization of water at 20° C. is 584.9 cal. per gram, which is equivalent to 10.53 kcal. per mole. Bernal and Fowler (4) have calculated that in the melting of ice the breaking of one-eighth of the hydrogen bonds would account for the latent heat of fusion. Similarly, to account for the specific heat, one bond in four would be broken at 100° C. So it may be assumed that in liquid water at 20° C. there is an open structure in which the oxygen molecules are united on the average by 3.4 bonds (i.e., 1 bond in 8 must be broken to account for the latent heat of fusion and 1 bond in 40 to account for the specific heat between 0° and 20° C.). Therefore in evaporating one water molecule it would be necessary on the average to break 1.7 hydrogen bonds, since the bonds are common to two molecules. To evaporate a gram-molecule of water would require 4.5 × 1.7 = 7.65 kcal. per gm. simply to disrupt the hydrogen bonds. (Presumably the 10.53 − 7.65 = 2.88 kcal. per gram-mole that remain in the heat of evaporation are due to van der Waals' and dipole forces.)

On the other hand, let us examine the possible means by which the water molecule may be attached to the cellulose molecule. Cellulose has the formula $(C_6H_{10}O_5)_n$, and the unit arrangement may be represented as follows:



These units are united in long chains of several hundred to form the cellulose molecules, and in turn these molecules are joined together to form the cellulose fibres. Presumably the link between the different molecules is made through a hydrogen bond, the oxygens in two of the side chains being joined through a hydrogen atom.

It is justifiable to assume that the water molecule is adsorbed on the cellulose molecule by means of two hydrogen bonds connecting the oxygen in the water molecule to two of the oxygen atoms in the side chains on the cellulose molecule. This water would thus be linked with two hydrogen bonds per molecule instead of the 1.7 bonds as calculated for liquid water. This represents an energy of 1.35 kcal. per mole or 75 cal. per gm. This value is of the same order as the excess that was found for the heat of adsorption in Fig. 5. It is very probable also that the hydrogen bonds in this case will have an energy greater than 4.5 kcal. per mole, as the configuration of the oxygen molecules affects the strength of the bond. Thus, in the aliphatic alcohols the hydrogen bond has an energy of 6.2 kcal. per mole. It seems therefore that a mechanism of this nature is quite adequate to explain the heat of adsorption found for the water originally adsorbed on the cellulose.

There are two other observational facts that will help us to form a complete picture of the adsorption phenomenon. In the first place it is well known that when wood or other cellulosic substance adsorbs water, the adsorption is accompanied by an expansion in the physical dimensions of the material, that is to say, swelling takes place. Second, water vapour has been found to diffuse much more easily than other gases through some materials. Thus rubber is over 50 times more permeable to water vapour than to hydrogen, and cellulose products themselves, such as paper or wood, transmit water much more quickly than air. This indicates that water molecules can move through these materials with a greater ease than would be expected from a consideration of the relative sizes of the molecules. In other words there appear to be very good grounds for believing that water molecules can enter small cracks or crevices that much smaller atoms cannot.

These two facts fit together very well to give an idea of what happens to the water molecule when it is adsorbed. It has been shown by X-ray analysis that cellulose swollen in water has the same crystal dimensions as normal cellulose. Hence the swelling must take place between the crystals. It has been pointed out here that the cellulose crystals are most probably joined together by hydrogen bonds. If this is so, the water molecules might enter between the crystals, breaking the hydrogen bonds joining the cellulose molecules, and replacing them by bonds between the water molecules and the two cellulose molecules. The insertion of the water would push the cellulose molecules apart and cause the expansion of the material as a whole. Also, since water molecules can force themselves between cellulose crystals in this way, they can move through materials that are impermeable to other gases not having this property.

The fact that the water molecule is able to force itself between cellulose crystals where other smaller molecules cannot enter is sufficient in itself to explain the volume contraction found when moisture is adsorbed by these substances. For in the experimental work that shows this contraction the assumption is made that the true volume of the cellulose is given by density measurements in helium. If however the water molecules can penetrate between the crystals into void spaces that are closed to helium then the true volume of the cellulose would not be given by the helium measurements. However, a conception of this nature is not satisfactory as an explanation of the volume compression occurring in certain aqueous solutions, such as sulphuric acid, and since the dilution of solutions is very similar thermodynamically to adsorption it is probable that the adsorbed water actually is arranged in a much closer structure in the adsorbed state than in the free liquid. In making the density measurements in water, the volume of the water adsorbed is lost, since it has entered spaces within the cellulose structure that were not available to the helium atoms. If it were not for the fact that these molecules of adsorbed water push the cellulose fibres apart and cause swelling, there would be no evidence on the basis of the usual type of measurements that they occupied any volume at all. The volume that is actually measured as occupied by the adsorbed water is the expansion of the cellulose structure. On the basis of this conception the expansion would be equal to the volume occupied by the adsorbed water. Unfortunately, however, because of the fact that cellulose has a sponge-like structure with internal air spaces, a measure of the expansion of the external physical dimensions does not reveal the total volume expansion since some of this expansion takes place in the internal air spaces. However, a qualitative relation might be expected between the volume occupied by the adsorbed water and the expansion. Collins (7) did find such a relation from the variation with temperature of the swelling of cotton hairs and the volume contraction as measured by Davidson (8), but he concludes that his measurements were "not capable of yielding any quantitative information as to the variation or significance of the value of the apparent specific volume of the adsorbed water." Thus, while there is no direct support for such a hypothesis, the available evidence does not seem to contradict it.

The observations made above naturally do not refer to capillary-adsorbed water since this water is obviously condensing in capillaries, which are accessible to helium gas. In that case there is no reason to believe that the volume occupied by water is other than that which one should expect it to occupy under such conditions. However, it must be realized that the different types of adsorption are not sharply separated but overlap and occur concurrently. Capillary adsorption and molecular adsorption between the cellulose crystals will take place simultaneously, and therefore it is exceedingly difficult to disentangle the effects.

Conclusion

The above discussion of the adsorption of water vapour by cellulose presents the following picture of the phenomenon:

1. The adsorption isotherm may be explained for a small region at low humidities by adsorption in a monomolecular layer obeying Langmuir's equation. In the region between 20 and 80% relative humidity the adsorption agrees with the polymolecular theory of Brunauer, Emmett, and Teller but a monomolecular theory assuming a decrease in attraction as the number of adsorbed molecules increases is not thereby excluded. In the region between 80% relative humidity and saturation it seems necessary to assume that capillary adsorption is predominant.

2. The heats of adsorption taken from various sources are found to give fairly consistent values, and when these heats of adsorption are plotted against the relative humidity the results obtained with cotton do not differ appreciably with those obtained with wood. When the heats of adsorption are compared with the free energy it is found that an extra energy term is

involved in the heat of adsorption, and this is assumed to be caused by an increased internal energy in the adsorbed state.

3. The study of the possible ways in which the water molecules may be attached to the cellulose crystals has shown that the increased energy of adsorption may be accounted for by assuming that the water molecules are attached to the cellulose by two hydrogen bonds. By considering the three dimensional arrangement of the cellulose molecule it should be possible to account for the contraction in volume that occurs during adsorption, and also to relate this to the swelling of the cellulose.

References

1. ARGUE, G. H. and MAASS, O. Can. J. Research, 12 (4) : 564-574. 1935.
2. BARKAS, W. W. Proc. Phys. Soc. London, 49 : 237-242. 1937.
3. BARKAS, W. W. Dept. Sci. Ind. Research (Brit.), Forest Products Research, Special Rept. No. 4. 1938.
4. BERNAL, J. D. and FOWLER, R. H. J. Chem. Phys. 1 : 515-548. 1933.
5. BRUNAUER, S., EMMETT, P. H., and TELLER, E. J. Am. Chem. Soc. 60 (2) : 309-319. 1938.
6. CAMPBELL, W. B. Dept. Interior, Canada, Forest Service Bull. 84. 1933.
7. COLLINS, G. E. J. Textile Inst. 21 : T311-T315. 1930.
8. DAVIDSON, G. F. J. Textile Inst. 18 : T175-T186. 1927.
9. FILBY, E. and MAASS, O. Can. J. Research, 7 (2) : 162-177. 1932.
10. FILBY, E. and MAASS, O. Can. J. Research, B, 13 (1) : 1-10. 1935.
11. KATZ, J. R. Kolloidchem.-Beihefte, 9 : 1-182. 1917.
12. LANGMUIR, I. J. Am. Chem. Soc. 40 (9) : 1361-1403. 1918.
13. NEALE, S. M. and STRINGFELLOW, W. A. Trans. Faraday Soc. 37 : 525-532. 1941.
14. PAULING, L. The nature of the chemical bond. Cornell University Press, Ithaca, N.Y. 1939.
15. PIDGEON, L. M. and MAASS, O. J. Am. Chem. Soc. 52 (3) : 1053-1069. 1930.
16. ROBERTS, J. K. Some problems in adsorption. Cambridge University Press. 1939.
17. RUSSELL, J. K., MAASS, O., and CAMPBELL, W. B. Can. J. Research, B, 15 (1) : 13-37. 1937.
18. STAMM, A. J. Ind. Eng. Chem. 30 (11) : 1280-1281. 1938.
19. STAMM, A. J. and HANSEN, L. A. J. Phys. Chem. 41 : 1007-1016. 1937.
20. STAMM, A. J. and LOUGHBOROUGH, W. K. J. Phys. Chem. 39 : 121-132. 1935.
21. STAMM, A. J. and SEBORG, R. M. J. Phys. Chem. 39 : 133-142. 1935.
22. URQUHART, A. R. and WILLIAMS, A. M. J. Textile Inst. 15 : T559-T572. 1924.
23. WILLIAMS, A. M. Proc. Roy. Soc. Edinburgh, 37 : 161-172. 1917.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. A. OCTOBER, 1942 NUMBER 10

ABSORPTION PHENOMENA IN A CONDENSED SPARK SOURCE[1]

By G. O. Langstroth[2] and W. W. Brown[3]

Abstract

Intensity ratios of certain line pairs in the spectrum of magnesium, of mercury, and of tin have been found to depend strongly on the amount of the element introduced into the source, even when the amount is within the range dealt with in making "trace" analyses. Line pairs involving transitions to a level in the ground term and to a considerably higher level exhibited this behaviour. It is attributed to the occurrence of partial absorption, mainly within the limits of the discharge. The dependence of the intensity ratios on the amount of the element present was not affected appreciably by air currents of 80 cm. per sec. velocity; it was affected however by currents of 1500 cm. per sec. velocity. The data lead to the conclusion that the absorption effects are normally quite stable, and are unlikely to introduce serious errors in analytic determinations.

Although considerable information, both experimental and theoretical, is available concerning the absorption of radiation in passing through layers of vaporized material (see, for example, (10)), little is known of the details of absorption in the arc or spark at atmospheric pressure. This is particularly true of sources used under conditions normally encountered in spectrographic analysis. It appeared desirable to investigate absorption phenomena for radiation from elements present in the source in extremely small amounts, and particularly to ascertain whether they are subject to fluctuations capable of introducing serious errors in analytic determinations.

In general, radiation involving a transition to a level in the ground term of an atom may be expected to exhibit self-absorption after passing through layers of the discharge, through a relatively cold cloud of vapour about the discharge, or through both. Such radiation is usually associated with spectral lines selected for measurement in making "trace" analyses, i.e., sensitive lines. On the other hand, radiation associated with higher final levels may be expected to suffer much less absorption for two reasons, (*a*) the populations of the higher atomic levels are small compared to that of the ground state in the discharge itself, and (*b*) cold vapour surrounding the discharge is highly transparent to the radiation. On this basis the intensity ratios of suitably chosen line pairs should depend on the amount of the element present in the source; the dependence should disappear when absorption effects become negligible.

---

[1] *Manuscript received July 1, 1942.*
Contribution from the Physics Department, University of Manitoba, Winnipeg, Man.

[2] *Associate Professor of Physics.*

[3] *Holder of a Bursary under the National Research Council of Canada.*

This article describes a study of the dependence of selected intensity ratios in the spectrum of magnesium, of mercury, and of tin, on the amount of the element present on the source electrode. A common type of condensed spark source was used. The investigated range extended from 4×10^{-7} to 8×10^{-4} mg. per mm.^{2} (of electrode surface) for magnesium, from 2×10^{-5} to 8×10^{-4} mg. per mm.^{2} for mercury, and from 8×10^{-6} to 8×10^{-4} mg. per mm.^{2} for tin. In the lower limit the deposit on the electrode approached the least quantity detectable. In addition, experiments were performed with an air blast directed against the source, in an attempt to influence the absorption phenomena. Air currents of 80 cm. per sec. velocity had little or no effect, but currents of 1500 cm. per sec. velocity influenced the dependence of intensity ratios on the amount of the element present.

1. Experimental

The condensed spark source in which the samples were excited was similar to that used by Langstroth and Newbound (8). The primary voltage of the power transformer was controlled by an autotransformer; in operation it was adjusted to the minimum value consistent with the passage of a single spark across the gap on every half cycle of the line voltage. Copper electrodes of the point-movable-plane type (2) were used. The area of the plane electrode was 1.0×1.3 cm.^{2}, and the electrode separation was 2.5 mm.

Spectra were photographed with a medium quartz spectrograph constructed at the University (slit width used, 60 microns). In order that intensity ratios of lines differing considerably in intensity might be determined from a single spectrum, a narrow antimony–quartz weakener (6) was placed over the central portion of the spectrograph slit. As a result, each spectral line on the plate exhibited a central section of decreased density in which photometric measurement on strong lines was possible. A magnified image of the discharge was formed in the plane of the slit with a quartz–fluorite lens. The intensity of light falling on the slit was adjusted to the desired value for each set of conditions by inserting an appropriate screen weakener immediately behind the condensing lens.

In order to study the dependence of the relative intensities of selected magnesium lines on the amount of magnesium present on the electrode, a graded series of aqueous solutions of magnesium chloride hexahydrate was prepared. Each solution contained 40 mg. per cc. of potassium acetate to act as a "buffer". The magnesium content ranged from 0.0010 mg. per cc. to 2.0 mg. per cc. Since 0.050 cc. of each solution was placed on a plane electrode and dried under reduced pressure, the magnesium content of the deposits ranged from 4×10^{-7} to 8×10^{-4} mg. per mm.^{2} of electrode surface.

Each of the prepared electrodes was sparked for 30 sec., and the spectrum was photographed. During the exposure the plane electrode was so moved that the base of the discharge passed once over the electrode surface, continually advancing to a fresh deposit. Use of the appropriate screen weakener for each sample, together with the antimony weakener, permitted the photographic density of the selected lines to be kept on the normal exposure portion of the characteristic curve of the plate. Calibration spectra were photographed on each plate with the aid of a brass arc operated at constant current and arc length, and a rotating step-sector (eight steps).

A similar procedure was adopted in the investigation of intensities in the mercury and in the tin spectrum. The amount of mercury in the electrode deposit was varied from 2×10^{-5} mg. per mm.^{2} to 8×10^{-4} mg. per mm.^{2}, and of tin from 8×10^{-6} mg. per mm.^{2} to 8×10^{-4} mg. per mm.^{2}

Intensity measurements were made by means of a microphotometric method (for details see (9)). Since the relative intensities for a particular plate were determined in terms of intensities of various lines in the calibration spectra for that plate, comparison with the results for another plate was made through spectra of samples common to both. By overlapping the concentration ranges in series of samples taken on different plates it was possible to express all results in the same arbitrary units. Intensities of strong lines were determined from measurements on the central "weakened" portion of a spectrum; intensities of the fainter lines were determined from measurements on the "unweakened" portions on either side, and the mean value was taken. Background corrections were made when necessary by determining the intensity of the background in the vicinity of the line, and subtracting it from the measured "line plus background" intensity. The magnitude of this correction increased with decreasing concentration of the element in the sample because of the progressively greater transmission required for the screen weakener. For this reason, the results obtained with very low concentrations are less accurate. It is believed that the intensity ratios are in error by less than 7%, except for the lowest concentrations where there may be errors of 10%.

To study the effect of an air blast on the absorption phenomena, the experiments were repeated with an air jet directed against the source. The air passed through a dust filter, a needle valve, and finally through a Pyrex tube placed horizontally and at right angles to the optic axis of the collimator. With this arrangement, light from the luminous tail which appeared on the discharge did not enter the spectrograph slit. The air velocity was estimated from subsidiary experiments by observation of the rate of displacement of water in a large container. Experiments were performed with air velocities of 80 cm. per sec., and 1500 cm. per sec.

The origin of the magnesium, mercury, and tin lines studied is indicated in the partial energy level diagrams of Figs. 1 and 2 (1, 3, 4, 5). Several of the lines measured were blends, owing in part to the low resolution of the spectrograph used with a relatively wide slit. It is believed that this circumstance does not detract seriously from the results. The blends were:

Mg 2937 Å. This was a blend of Mg I 2936.895 Å and Mg II 2936.537 Å. The intensity of the latter is estimated to be slightly the greater (4).

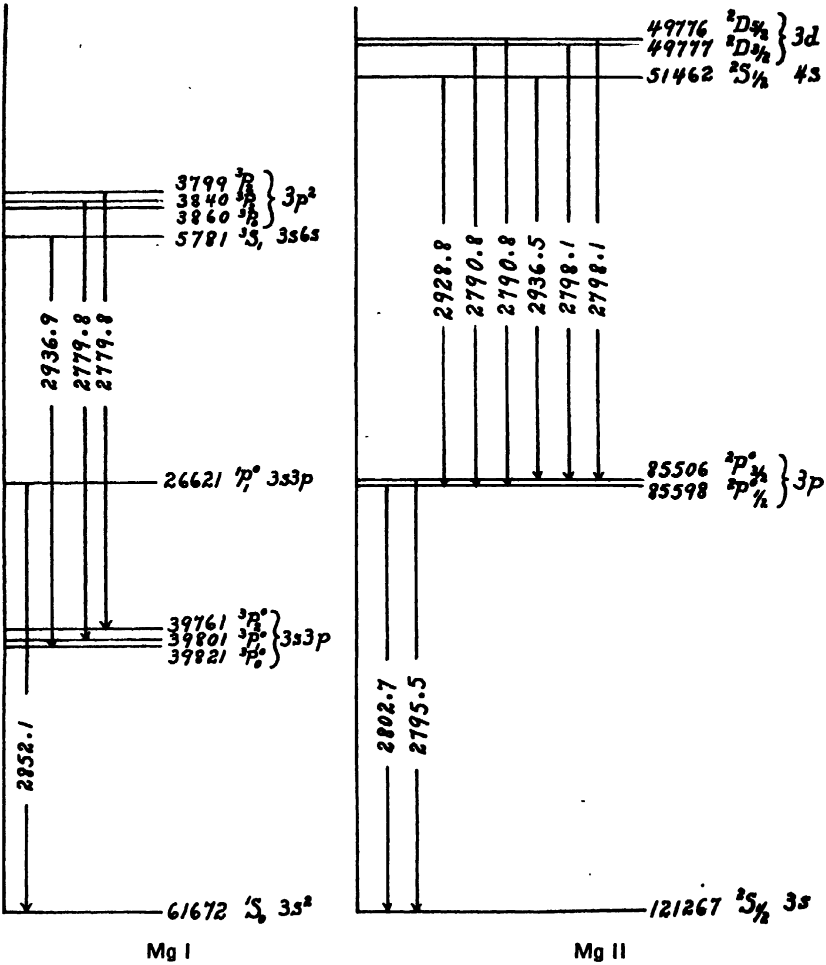


FIG. 1. *Partial energy level diagram for magnesium.*

Both lines however involve final levels far above the ground level of the atom and ion (21851 and 35761 cm.$^{-1}$ respectively).

Mg I 2780 Å. This was a blend of $3s3p\,^3P^0_1 - 3p^2\,^3P_1$ and $3s3p\,^3P^0_2 - 3p^2\,^3P_2$, both having a wave-length of 2779.834 Å. Both initial and final levels lie close together (separations 40.6 and 40.9 cm.$^{-1}$ respectively).

Mg II 2791 Å. This was a blend of $3p\,^2P^0_{1/2} - 3d\,^2D_{5/2}$ and $3p\,^2P^0_{1/2} - 3d\,^2D_{3/2}$, both having a wave-length of 2790.787 Å. They have a common final level and the initial level separation is small.

Mg II 2798 Å. This was a blend of $3p\,^2P^0_{3/2} - 3d\,^2D_{5/2}$ and $3p\,^2P^0_{3/2} - 3d\,^2D_{3/2}$, both having a wave-length of 2798.06 Å. They have a common final level and the initial level separation is small.

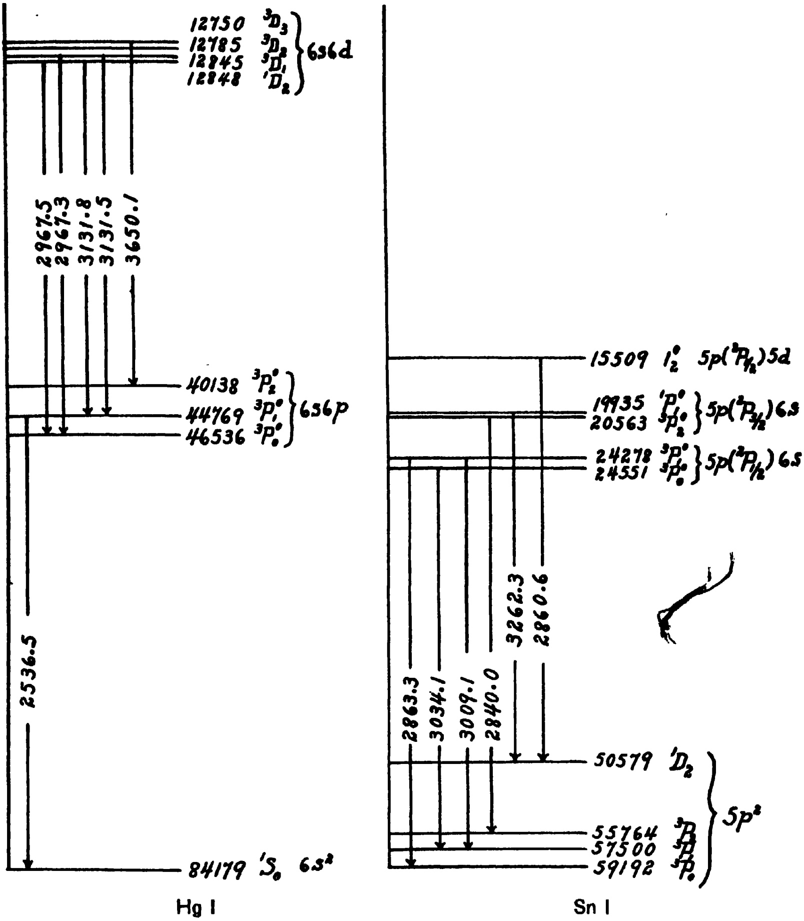


FIG. 2. *Partial energy level diagrams for mercury and tin.*

Hg I 2967 Å. This was a blend of 2967.278 Å, 2967.517 Å, and 2967.592 Å, with estimated intensities (4) respectively 100, 5, and 10. The first two have a common final level and small initial level separation; the classification of the last, which contributes only a small part to the combined intensity, is unknown to the writers.

Hg I 3132 Å. This was a blend of 3131.546 Å and 3131.833 Å. These lines have a common final level and the initial level separation is small.

2. Results

(a) Results obtained in still air. Data describing the dependence of the intensity ratios on the amount of the element present on the electrode are given in Tables I (Mg), II (Hg), and III (Sn). The results for each element

represent a separate series of experiments. The ratios for the greatest deposit of the element have been set equal to 100. In all ratios the numerator is the line having the higher final level. The line pairs are arranged to involve progressively higher atomic levels as one proceeds toward the right-hand side of the tables.

TABLE I

DEPENDENCE OF INTENSITY RATIOS OF Mg I AND Mg II LINE PAIRS ON THE AMOUNT OF MAGNESIUM PRESENT ON THE ELECTRODE. THE DATA WERE OBTAINED IN STILL AIR

Mg on the electrode, mg. per mm.^{2} ($\times 10^6$)	Mg I			Mg II							
	$\frac{2937}{2852}$	$\frac{2780}{2852}$	$\frac{2780}{2937}$	$\frac{2796}{2803}$	$\frac{2929}{2803}$	$\frac{2791}{2803}$	$\frac{2798}{2803}$	$\frac{2929}{2796}$	$\frac{2791}{2796}$	$\frac{2798}{2796}$	$\frac{2791}{2798}$
800	100	100	100	100	100	100	100	100	100	100	100
400	68	75	113	106	82	76	76	79	73	72	100
200	50	66	130	—	62	62	64	—	—	—	97
80	34	44	150	105	52	47	54	51	45	40	108
40	33	38	120	114	42	39	42	40	37	33	114
8	15	21	140	140	35	29	33	26	22	24	112
5.3	—	—	—	140	32	29	26	24	21	23	108
4.0	12	14	111	140	30	26	23	22	19	20	112
2.7	9.5	11	104	130	32	24	23	24	18	17	109
0.8	9.4	9.3	—	140	—	25	18	—	17	13	130
0.4	—	—	—	140	—	25	20	—	19	13	—

TABLE II

DEPENDENCE OF INTENSITY RATIOS OF Hg I LINE PAIRS ON THE AMOUNT OF MERCURY PRESENT ON THE ELECTRODE. THE DATA WERE OBTAINED IN STILL AIR

Hg on the electrode, mg. per mm.^{2} ($\times 10^6$)	Hg I				
	$\frac{2967}{2537}$	$\frac{3132}{2537}$	$\frac{3650}{2537}$	$\frac{3132}{2967}$	$\frac{3650}{2967}$
800	100	100	100	100	100
400	64	56	63	88	99
200	27	27	29	101	108
80	19	18	20	98	106
40	15	17	16	117	106
20	16	15	14	93	84

(b) Results obtained with an air blast. Results obtained with air blasts of 80 cm. per sec. and 1500 cm. per sec. are shown in Figs. 3, 4, and 5, where they are compared with the results obtained in still air.

3. Discussion

The data of Tables I, II, and III show a marked dependence of the intensity ratios of certain line pairs on the amount of the element present on the electrode. For example, the ratio for Mg I 2780/2852 increased by a factor

TABLE III

DEPENDENCE OF INTENSITY RATIOS OF Sn I LINE PAIRS ON THE AMOUNT OF TIN PRESENT ON THE ELECTRODE. THE DATA WERE OBTAINED IN STILL AIR

Sn on the electrode, mg. per mm.^{2} ($\times 10^6$)	Sn I					
	$\frac{3034}{2863}$	$\frac{3009}{2863}$	$\frac{2850}{2863}$	$\frac{3262^*}{2863}$	$\frac{3009}{3034}$	$\frac{2850}{3262^*}$
800	100	100	100	100	100	100
400	100	94	85	98	92	87
200	104	90	66	93	85	71
80	97	84	59	87	84	68
20	100	82	55	82	81	66
8	105	91	51	76	88	67

* *There may have been a systematically varying error in the measurement of the intensity of his line, as pointed out in the discussion.*

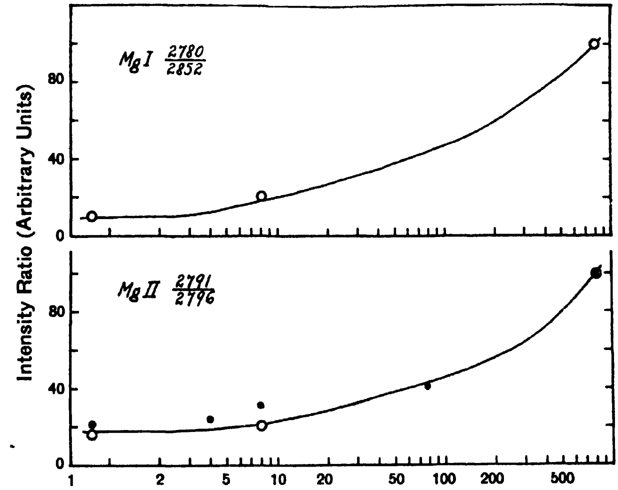


FIG. 3. *The effect of an air blast on the curves for intensity ratios vs. amount of magnesium on the electrode. The solid lines represent the data obtained in the absence of an air blast; individual values, which are given in Table I, are not indicated on the graph. Values obtained with an air current of 80 cm. per sec. velocity are indicated by* ○; *those obtained with a current of 1500 cm. per sec. velocity are indicated by* ●.

of 11 when the amount of magnesium on the electrode was increased from 8×10^{-7} mg. per mm.^{2} to 8×10^{-4} mg. per mm.^{2} On the other hand, certain other line pairs showed no evidence of such behaviour. Line pairs having one final level in the ground term and the other considerably above it belong without exception to the former class; those involving close lying final levels, whether these levels be in the ground term or not, belong to the latter class. An apparent exception occurs for the Sn I line pair 2850/3262. These lines

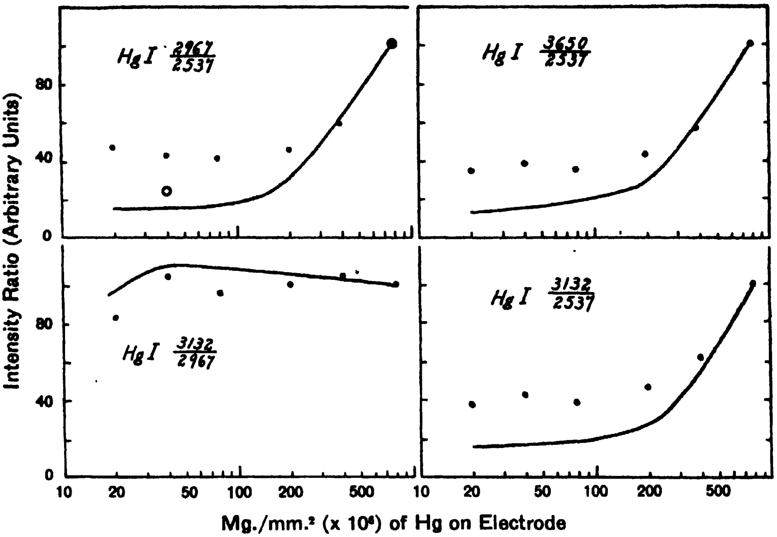


FIG. 4. *The effect of an air blast on the curves for intensity ratios vs. amount of mercury on the electrode. As in Fig. 1, the solid line represents the data obtained in the absence of an air blast. Intensity ratios obtained with an air current of 80 cm. per sec. are indicated by* ○; *ratios obtained with a current of 1500 cm. per sec. are indicated by* ●.

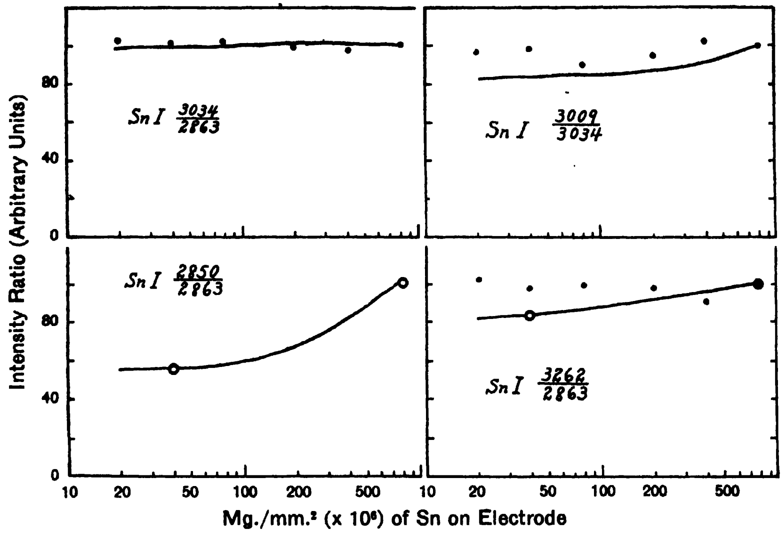


FIG. 5. *The effect of an air blast on the curves for intensity ratios vs. amount of tin on the electrode. The solid line represents the data obtained in the absence of an air blast, and* ○ *and* ● *represent intensity ratios obtained with air currents of 80 cm. per sec. and 1500 cm. per sec. respectively.*

have a common final level, yet their intensity ratio decreased with decreasing amount of tin on the electrode. The initial levels are separated by 4426 cm.$^{-1}$. The observed decrease may be spurious, for the following reason. The line 3262 Å lies between the copper lines at 3247 Å and 3274 Å—the strongest lines in the copper spectrum. Hence the background intensity for 3262 Å was difficult to determine accurately. As the amount of tin on the electrode was decreased, screen weakeners of progressively higher transmission were used, with the result that the photographic density of lines of the copper spectrum on the plate became great. Underestimation of the background intensity for 3262 Å would produce data involving 3262 Å similar to those observed.

With the apparent exception just noted, the picture presented by the data is that to be expected from the occurrence of appreciable absorption. The observed intensity changes in the spectra of Mg I, Mg II, and Hg I are similar, as might be expected from the similarity of the energy level diagrams. They are probably almost entirely due to partial absorption of the 2852 Å, 2803 Å, 2796 Å, and 2537 Å radiation. Partial absorption of lines having final levels considerably above the ground state must be relatively unimportant. On the other hand, it is probable that all the investigated tin lines are affected to some extent by absorption, those ending on the $5p^2\ {}^1D_2$ level being least influenced. The basis for these expectations lies in a comparison of the estimated relative populations of various final levels for an assumed Boltzman distribution (see (7)) at a temperature of 6000° K. (Table IV). The mean "effective" temperature of the absorbing region of vapour is probably no higher than 6000° K., if as high.

TABLE IV

ESTIMATED RELATIVE POPULATIONS OF FINAL LEVELS FOR A BOLTZMAN DISTRIBUTION AT 6000° K.

Element	Level	Relative population	Element	Level	Relative population
Mg	$3s^2\ {}^1S_0$	1000	Hg	$6s^2\ {}^1S_0$	1000
(neutral atom)	$3s3p\ {}^3P_0^0$	5		$6s6p\ {}^3P_0^0$	0.1
	$3s3p\ {}^3P_1^0$	15		$6s6p\ {}^3P_1^0$	0.2
	$3s3p\ {}^3P_2^0$	25		$6s6p\ {}^3P_2^0$	0.1
(ion)	$3s\ {}^2S_{1/2}$	1000	Sn	$5p^2\ {}^3P_0$	1000
	$3p\ {}^2P_{1/2}^0$	0.2		$5p^2\ {}^3P_1$	2000
	$3p\ {}^2P_{3/2}^0$	0.3		$5p^2\ {}^3P_2$	2200
				$5p^2\ {}^1D_2$	650

Curves for intensity ratios of "variable" line pairs plotted on log-log paper against the amount of the element present on the electrode are concave upwards, the slope tending toward zero as the amount decreases. They indicate that in the region of 2×10^{-6} mg. per mm.^{2} of magnesium, and of 2×10^{-5} mg. per mm.^{2} of mercury, absorption effects become relatively unimportant, i.e., the ratios tend to reach a constant value. These amounts involve approximately equal numbers of atoms. They approach the least quantities of magnesium and mercury detectable with this source.

A simple calculation shows that the amount of an element (as vapour) effective in producing detectable absorption must be extremely minute. For example, from Table I, Mg I 2852 Å was markedly absorbed when the amount of the element on the electrode was as small as 10^{-5} mg. per mm.^{2}. Assuming one-quarter of the deposit to be removed in sparking for 30 sec. (a high upper limit), and to be distributed with spherical symmetry about the source, the average amount of magnesium present in the solid angle subtended by the condensing lens comes out to be about 6×10^{-7} mg. The data obtained with an air blast directed against the discharge give reason to believe that this figure is far too high.

Results partially presented in Figs. 3, 4, and 5 indicate that air currents of 80 cm. per sec. velocity had little or no effect on the absorption phenomena. Air currents of 1500 cm. per sec. velocity did reduce the absorption, but not to the extent that might be expected if the principal absorbing medium was a cloud of cool vapour collected about the source. Air velocities of 80 cm. per sec. would move such a cloud a distance of about 0.7 cm. in the interval between sparks (1/120 sec.), while air velocities of 1500 cm. per sec. would move it about 12 cm. The failure of the air blasts to produce more marked effects suggests that the absorption takes place largely within the limits of the discharge itself, and that for radiation from a single spark, it is caused mainly by material released during that spark and possibly a few preceding ones. On this basis, collection of cool vapours about the discharge plays a relatively minor role.

Because of the occurrence of absorption phenomena in the concentration range of interest in making trace analyses, the working curves for lines with high final levels may differ markedly in character from those for lines with low final levels, as may be inferred from the results of Tables I, II, and III. Providing the phenomena are not subject to appreciable fluctuations this is not a serious matter. The results discussed above show that the phenomena are remarkably "stable". They indicate that no appreciable errors are introduced in analytic determinations by variations in absorption due to varying air currents of velocities commonly encountered in the laboratory.

References

1. Bacher, R. F. and Goudsmit, S. Atomic energy states. McGraw-Hill Book Company, Inc., New York and London. 1932.
2. Foster, J. S., Langstroth, G. O., and McRae, D. R. Proc. Roy. Soc. (London) A, 153 : 141-152. 1935.
3. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922.
4. Harrison, G. R. Massachusetts Institute of Technology wavelength tables. J. Wiley and Sons, Inc., New York. 1939.

5. **Kayser**, H. and **Konen**, H. Handbuch der Spectroscopie. Vol. 7. S. Hirzel, Leipzig. 1930.
6. **Langstroth**, G. O. and **McRae**, D. R. Can. J. Research, A, 15(9) : 154-160. 1937.
7. **Langstroth**, G. O. and **McRae**, D. R. Can. J. Research, A, 16(1) : 17-27. 1938.
8. **Langstroth**, G. O. and **Newbound**, K. B. Can. J. Research, A, 20(4) : 39-47. 1942.
9. **Langstroth**, G. O., **Newbound**, K. B., and **Brown**, W. W. Can. J. Research, A, 19(7) : 103-108. 1941.
10. **Mitchell**, A. C. G. and **Zemansky**, M. W. Resonance radiation and excited atoms. The University Press, Cambridge. 1934.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. NOVEMBER, 1942 NUMBER 11

LIBRAR

SECONDARY RADIATION FROM X-RAY FILTERS

I. SINGLE-METAL FILTERS[1]

BY G. A. WRENSHALL[2] AND H. J. NICHOLS[3]

Abstract

Using an ionization chamber method, the intensity distribution and quality of forward transmitted secondary X-rays from filters of aluminium, copper, tin, and lead have been measured under standard operating conditions. Geometrical arrangements of X-ray tube, defining apertures, filter, and receiver commonly used in medical and industrial radiology are employed. Suggestions for minimizing the intensity of the secondary radiation reaching the receiver from single-metal filters are submitted.

Introduction

While considerable study has been made of the secondary X-radiation emitted from absorbing foils, most investigators have studied only the portion of the radiation emitted on the incident side of the foil (1, 4, pp. 121, 125, 142). There is, however, practical interest in information concerning the forward transmitted secondary radiation since the distribution, hardness, and intensity of this radiation relative to that of the primary beam is found to be of importance in X-ray therapy and radiography where filters are employed. Since the transmitted primary beam is generally of much greater intensity than the forward transmitted secondary radiation produced by it, it is difficult to make accurate measurements of that part of the secondary radiation mixed with the transmitted primary beam. For this reason the secondary radiation falling just outside of the transmitted primary beam was examined in this investigation.

Seemann (6) has made an experimental study of the intensity distribution of the forward transmitted secondary X-rays from a filter as a function of certain variables in the geometry of his apparatus, which was arranged to simulate the conditions actually encountered where X-ray filtration is used. He has compared his measurements with calculations based on certain assumptions concerning the origin of the secondary X-rays. However, his most interesting measurements designed to test these calculations were made, not with secondary X-rays produced by an absorbing filter, but with light scattered by a ground-glass screen and detected with a light meter. The present paper deals in part with the direct measurement of the intensity distribution of secondary X-rays for the geometrical arrangements of source, filter, and detector suggested by Seemann as well as for other arrangements that were felt to be of practical importance.

---

[1] *Manuscript received in original form June 29, 1942, and as revised, August 24, 1942.*

Contribution from the Department of Physics, McMaster University, Hamilton, Ont., with financial assistance from the National Research Council of Canada.

[2] *Lecturer in Physics, McMaster University.*

[3] *Graduate Research Student.*

Experiment

The geometrical conditions (Arrangements I and II) of apparatus employed in this study are illustrated in Figs. 1*a* and 1*b* respectively. In Arrangement I the cross-section of the primary X-ray beam from source S is maintained at

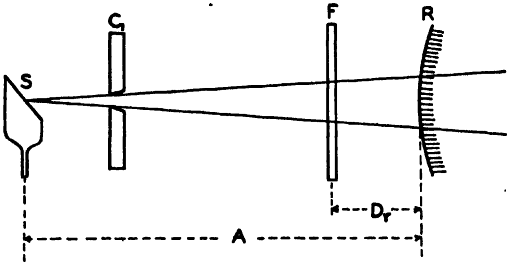


Fig. 1*a*.

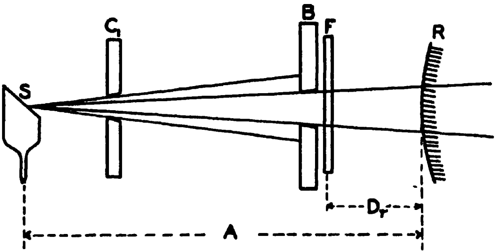


Fig. 1*b*.

FIGS. 1*a* AND 1*b*. *Basic geometrical arrangements of X-ray source S, apertures, B, C_1, filter, F, and receiver, R, as used in runs of Types I and II respectively.*

constant size by a collimator, represented simply as C_1. The primary beam is allowed to irradiate a receiver R placed at a constant distance A from S. The filter F, a foil of uniform thickness and sufficiently large in cross-section to fill the entire fixed cone of primary radiation at all positions, is inserted between S and R in a plane perpendicular to the direction SR. The intensity I_s of secondary radiation reaching R from F is then measured at various distances D_r of F from R. In Arrangement II, F is placed behind a lead aperture B, and the cross-section of the beam of primary X-rays is made sufficiently large to irradiate all of the exposed portion of F uniformly at all distances D_r of F from R, and D_r is varied with aperture B in contact with F in all positions.

The types of measurement made and reported in this paper are as follows:

(*a*) Using Arrangement II, I_s is measured for various thicknesses of *F*, but with D_r held constant, and for each of three peak voltages applied across the X-ray tube.

(*b*) The space rate of absorption in aluminium of the secondary X-rays from *F* is measured, and the quality of the secondary radiation is ascertained therefrom. The apparatus is arranged as in (*a*), but with the addition of a variable number of aluminium plates of known mass per unit area interposed between *F* and *W* and parallel to *F* (Fig. 2). Each plate has a sufficiently large aperture at its centre to allow the primary beam of X-rays to pass through to *C* unaltered, while all secondary rays from *F* directed toward *W* have to pass through the plates. Absorption curves are obtained for the secondary X-rays reaching the ionization chamber from *F*, and effective absorption coefficients are estimated, the corresponding wave-lengths being obtained from physical tables.

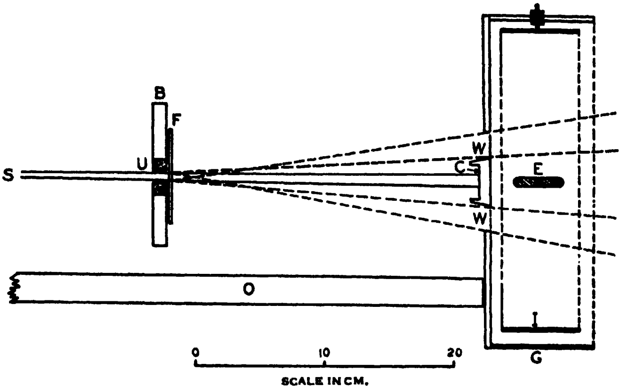


FIG. 2. *Side section of the ionization chamber, and its position relative to filter F and optical bench O.*

(*c*) Using a set of rotating sectored lead disks to reduce the intensity of the primary beam by a known fraction, measurement is made of the relative intensities of primary and secondary X-rays reaching *W* from *F* using Arrangement II as in (*a*).

(*d*) The observations made by Seemann are studied with X-rays for Arrangements I and II.

For the direct measurement of ionization of forward transmitted secondary X-rays in accordance with the geometrical conditions of Figs. 1*a* and 1*b*, the general disposition of apparatus shown schematically in Fig. 2 is employed. A collimated pencil of primary X-rays from a source *S* is allowed to pass through the absorbing filter *F* held against aperture *B*, and is finally blocked in a heavy lead cup *C* placed at the centre of the annular window *W* of a large flat cylindrical ionization chamber. Secondary X-rays originating in *F* enter and leave the inner ionization chamber *I* through aluminium foil windows, relative intensities being measured by means of the saturation ionization current between *I* and the central electrode *E*, which is suitably connected to a completely shielded quadrant electrometer. Dry air at room temperature and pressure is used in *I* for all measurements, facilitating direct comparison of results with standard intensity measurements.

Both medium-focus and fine-focus Coolidge radiation type X-ray tubes (tungsten anticathodes) are used as sources, the latter being employed in all measurements of Type (*d*) where ideal geometrical conditions require the use of a point source of X-rays. The source *S* is completely encased in a lead box, and is supplied by a standard mechanical rectifier type of high tension supply whose peak kilovoltage output was measured under operating conditions by means of a standard sphere-gap. A storage battery source of filament current is used, making it possible to hold the intensity of the primary X-ray beam constant to within 1.0% during the course of an entire run.

Since it was found in preliminary runs that a considerable intensity of the secondary K-radiation of lead was reaching *W* from the edges of defining aperture *B* when 100 kvp. X-rays were employed, the periphery of this aperture was replaced by a plug *U* of uranium oxide and binder. This greatly improved the condition since the K-radiation of uranium is not excited by X-rays of less than 115 kv., while those of lead require only 88 kv.

The materials used successively in filter *F*, namely, lead, tin, copper, aluminium, are those commonly employed, either singly or in combination, by radiologists in the filtration of X-rays for medical purposes. Each was of the highest available degree of purity, and with respective atomic numbers of 82, 50, 29, 13, the results and conclusions obtained from the study of these metals should be representative of all metal elements available for filter construction.

Certain operations in the measurement of secondary X-ray intensities were common to all runs. After every measurement with a new filter setting, *F* was restored to a standard condition of thickness and position on the optical bench *O*, where the constancy of the primary beam intensity was checked*. Secondly, a correction was made by a single measurement for the general background radiation entering the ionization chamber in various ways, and for the unavoidable residuum of secondary radiation originating in *U* and entering *W* after passing through *F*. A foil of the same material and thickness as *F* was placed directly over *W*, and *F* was removed, following which the total background intensity was measured. In this way the secondary radiation from *U* had to penetrate the same thickness of filter material as before, and hence was reduced in intensity by the same fraction before entering *W*. General background radiation on the other hand, originating mainly in *C* as the secondary K-radiation of lead, or entering *I* through the thin rear windows, was relatively unchanged by this operation.

---

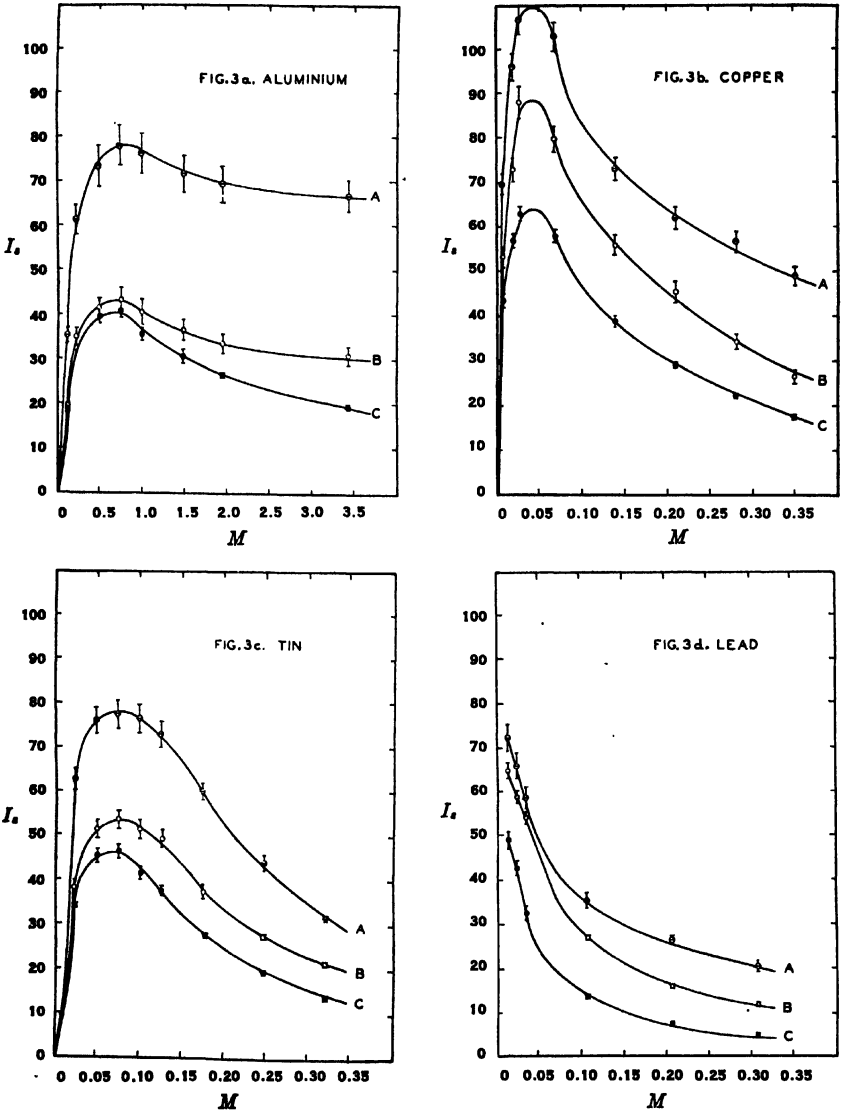
* *In all measurements relative intensities of secondary X-rays were considered to be proportional to the unaccelerated rate of deflection of the electrometer needle over a fixed portion of the electrometer scale.*

It will be observed from Fig. 2 that as F is moved along the axis of the primary X-ray beam, the mean angle θ, included between the primary beam axis and the secondary X-rays from F entering W, will vary between certain limits. Secondary radiation leaving F at an angle θ will be reduced in intensity by a factor $e^{-1/\cos\theta}$ when compared with equivalent radiation emitted at the same point in F and emerging normally to the foil ($\theta = 0$). However the first-mentioned beam will produce greater ionization in I than the second by a factor $1/\cos\theta$ due to its longer path in the ionization chamber. Since in the writers' measurements θ does not become greater than 10° these two factors annul each other's effect to within 0.001% for fluorescence secondary radiation, which is emitted without preferred direction at its source. Correction for the variation in intensity with θ of the scattered components of secondary radiation is not as complete in the apparatus as described, owing to different angular distribution of intensity (3).

Results

Measurements of Type (*a*) on the variation of secondary X-ray intensity with mass per unit area of filter are presented in Figs. 3*a* to 3*d* for aluminium, copper, tin, and lead respectively. Runs were made with X-ray tube voltages of 115, 100 and 85 kvp., corresponding to curves *A*, *B*, *C*, respectively, and with X-ray tube current held constant for each metal. With the exception of lead, it was found that in each case a certain thickness of filter existed at which the intensity of the forward transmitted secondary X-radiation was a maximum, an effect that has been observed by others for supervoltage X-rays (2). In the case of lead (Fig. 3*d*), it is doubtful whether the filter thickness yielding maximum intensity of secondary radiation was reached. Thinner lead foils with which to check this possibility were unavailable owing to war conditions. It may be observed that in each case the intensity of the secondary radiation reaching the receiver increases with increasing X-ray tube kilovoltage, and that for each of the three lighter metals the mass per unit area of filter required to give the secondary X-ray intensity maximum is relatively independent of the applied X-ray tube voltage for the voltage range considered. The secondary X-ray maxima were found to occur at 0.70, 0.04, and 0.07 gm. per cm.^{2} mass per unit area for aluminium, copper, and tin respectively, and for lead the corresponding mass per unit area is known to be less than 0.02 gm. per cm.^{2}

The quality of the secondary radiation from the various filters was examined in runs of Type (*b*). Observations were made for tin, copper, and aluminium. For tin and copper it was found that the effective absorption coefficients were considerably larger for small thicknesses of absorbing aluminium foils than for larger. Mass absorption coefficients fell from 1.7 cm.^{2} per gm. for tin and 12 cm.^{2} per gm. for copper to the common value of approximately 0.9 cm.^{2} per gm. as the thickness of the absorber increased. The wave-lengths associated with these figures indicate that in each case the secondary radiation consisted of a combination of the K-fluorescence radiation of the filter material plus a component of scattered radiation of effective wave-length corresponding to that of the primary X-ray beam. The ionizing power of the two components is approximately equally divided between the two types of radiation



FIGS. 3a TO 3d. *Curves illustrating trend of experimental observations relating I_s (arbitrary units) to mass per unit area M (gm. cm.$^{-2}$) of filter for runs of Type IV using aluminium, copper, tin, and lead filters respectively. Curves A, B, and C were obtained in each case using X-ray tube voltages of 115, 100, 85 kvp. respectively with X-ray tube current held constant for each filter.*

for both metals. The secondary radiation from aluminium proved to be more nearly homogeneous than that from tin and copper, with the same effective absorption coefficient as that obtained for these two metals with thick layers of aluminium absorber, namely, 0.9 $cm.^2$ per gm. The absence of more precise numerical values of effective absorption coefficients in this section of the experiment arises from the difficulty of accurately comparing, with the apparatus available, intensities of X-rays having different wave-length ranges.

In Type (*c*) runs, a measure of the relative intensities of primary and forward transmitted secondary radiation emerging from an aluminium filter F placed at a distance of 20 cm. from the ionization chamber was obtained. The corrected rate of electrometer needle deflection caused by secondary X-rays entering the ionization chamber was measured using the procedure already described, and will be designated as R_1. A set of rotating sectored disks (8) were then inserted between B and the X-ray source S, and the ionization chamber was shifted upwards sufficiently to allow the same beam of primary X-rays transmitted by F to pass through the ionization chamber window, following which the rate of deflection R_2 due to primary plus secondary X-rays was measured. The intensity of the primary plus secondary beam was reduced to a known fraction f of its full value by means of the sectored disks, so that R_1 and R_2 were of the same order of magnitude. If A_1 is the area of the window through which the secondary radiation reaches the ionization chamber, and A_2 the cross-sectional area of the primary beam as it enters the ionization chamber, the ratio I_s/I_p of the intensities of primary and secondary radiation entering the ionization chamber is given by the relation:

$$\frac{I_s}{I_p} = \frac{R_1A_2}{R_2A_1} f,$$

assuming that I_s is small compared to I_p.

For the aluminium filter tested under the above conditions, and with the X-ray tube operating at 100 kvp., a value of $\frac{I_s}{I_p} = 0.00029$ was obtained, which is found to increase to 0.15 at a distance of 1.0 cm. from the ionization chamber. Aluminium was chosen as the filter material in this measurement since it has been already observed that its secondary radiation has virtually the same effective wave-length as that of the primary X-ray beam, and hence difficulties arising out of a comparison of intensities where different wave-lengths are involved do not complicate the calculation. Similar runs were made with the other three metals, and it was found that under similar experimental conditions the ratio of secondary to primary intensities was of the same order of magnitude for each of these metals as for aluminium, although the heterogeneous secondary radiations obtained do not permit the statement here of significant numerical figures. In each case, filter masses per unit area that were found earlier to give the maximum intensity of secondary X-rays were used.

Results for runs of Type (*d*) for aluminium, copper, tin, and lead filters are presented in Figs. 4*a* and 4*b*, respectively. These are compared with the theoretical predictions made by Seemann, which are shown as full straight lines in each figure. It is observed that within broad limits substantial agreement exists between measured and predicted X-ray intensities for all the metals studied, with perhaps a minor exception in the case of lead. For practical purposes the point of main interest is well demonstrated: for all cases studied under actual operating conditions with X-rays, the lowest possible intensity of X-rays at the receiver is obtained when the filter is placed as close as possible to the source for Arrangement I, and when $D_r = \frac{A}{2}$ for Arrangement II.

Discussion

The existence of a maximum in each of the curves of Fig. 3 is to be expected on theoretical grounds, since a relation has been obtained and compared with experiment for scattered radiation alone (2); and it can be shown that a relation of the same form holds when only fluorescence radiation is considered. Were one of the objects of this paper an experimental study of the above predictions, it would be necessary to insure that the primary X-ray beam used be monochromatic, and that the relative intensities and wave-lengths of the fluorescence and scattered X-radiation be known. The purpose of this paper is rather to supply usable experimental information on the distribution of secondary X-ray intensities from commonly used filter materials under those geometrical conditions most generally used, and with a beam of primary X-rays having a spectral distribution of intensity corresponding to that used as a standard*. Hence attention is directed at present only toward attaining these working conditions with the equipment available.

With reference to Type (*d*) runs in particular, differences between predicted and observed results do not appear to be caused by employment of the rate of deflection method for comparison of intensities, although this method has been held by Richtmyer (5) to be unreliable when several-fold differences in intensity magnitude are compared. That our measurements are reliable in this respect was checked by reducing the intensity of the beam of primary X-rays by known amounts with the set of rotating sectored lead disks, and observing the degree of direct proportionality between intensity of primary radiation incident on a given filter and the corresponding rates of deflection of the electrometer needle. A coefficient of linear correlation of +0.99 was observed between these two variables for rates of deflection of the same order of magnitude as were used throughout the present study, indicating that our measurements are not subject to Richtmyer's criticism to any significant degree.

It has been observed in this study that the value of $\frac{I_s}{I_p}$ for a single-metal filter can be minimized by the proper placement of filter relative to source, receiver, and defining apertures, and by the avoidance of use of filters having

---

* *Radiologists use an X-ray tube current of 5.0 ma. at 100 kvp. as a standard reference setting. The X-ray tubes employed by most medical units have tungsten anticathodes. Taylor, Singer, and Stoneburner (7) find that X-ray qualities at a given effective voltage are nearly the same for all generators.*

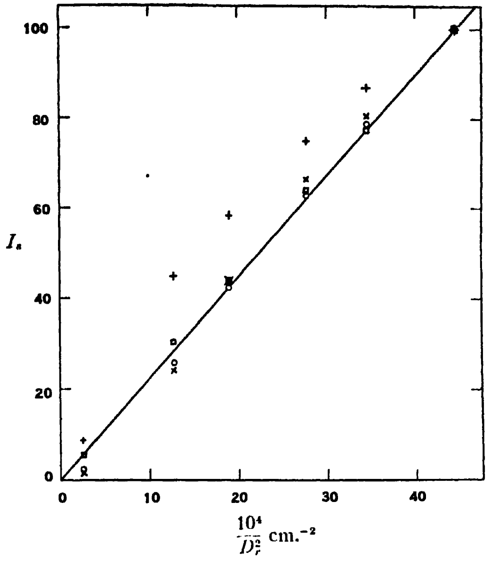


FIG. 4*a*

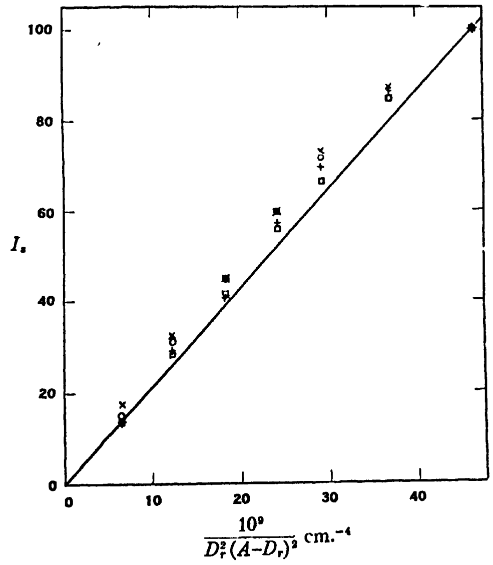


FIG. 4*b*

FIGS. 4*a* AND 4*b*. *Results for runs of Type (d), Arrangements I and II respectively. Seemann's analysis predicts that* $I_s = \frac{K_2}{D_r}$ *for Arrangement I, and that* $I_s = \frac{K'}{D_r^2(A - D_r)^2}$ *for Arrangement II (represented as a full line in each graph). Experimental points for aluminium, copper, tin, and lead are identified by the symbols:* ×, ○, ☐, +, *respectively.*

thicknesses such that a maximum value of $\frac{I_s}{I_p}$ is obtained, as found in runs of Type (*a*). It is found in practice that, aside from these factors, secondary radiation from certain single-metal filters still constitutes a real hindrance in photographic and therapeutic radiology, owing to the much higher space rate of absorption of the secondary than of the filtered primary radiation in the surface layers of the receiver. To reduce this effect, compound filters composed of laminae of various single metals have been employed. An experimental examination of the effectiveness of standard forms of such filters is at present in progress as a continuation of the present problem.

Acknowledgments

The authors wish to express their appreciation to Dean C. E. Burke and to Dr. L. R. Hess, Sr., for their continued advice, encouragement, and aid in obtaining the equipment with which this work is being carried on. They wish to acknowledge with thanks the loan of a set of rotating sectored lead disks by Prof. E. L. Harrington of the University of Saskatchewan. They also wish to thank Prof. A. B. McLay for valuable suggestions concerning the manuscript, and Mr. N. Morrow for assistance with some of the experimental work. One of the writers (H.J.N.) wishes to express his gratitude to the National Research Council of Canada for a Bursary held during the past year, enabling him to take part in this work.

References

1. BALDERSTON, M. Phys. Rev. (Ser. 2) 27 : 696-708. 1926.
2. CASSEN, B., CORRIGAN, K. E., and HADEN, H. S. Radiology, 31 : 319-324. 1938.
3. HEWLETT, C. W. Phys. Rev. (Ser. 2) 20 : 688-708. 1922.
4. KAYE, G. W. C. X-rays. Longmans, Green, and Co., London. 1917.
5. RICHTMYER, F. K. Phys. Rev. (Ser. 2) 30 : 755-761. 1927.
6. SEEMANN, H. E. Am. J. Roentgenol. Radium Therapy, 39 : 628-633. 1938.
7. TAYLOR, L. S., SINGER, G., and STONEBURNER, C. F. Am. J. Roentgenol. Radium Therapy, 30 : 368-379. 1933.
8. WRENSHALL, G. A. and HARRINGTON, E. L. Can. J. Research, A, 14(12) : 209-215. 1936.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. A. DECEMBER, 1942 NUMBER 12

NOTE ON THE ENERGY AND MOMENTUM CORRECTION FACTORS FOR FLOW IN CIRCULAR PIPES[1]

BY K. F. TUPPER[2]

Abstract

The energy and momentum correction factors are expressed as functions of two integrals depending on the velocity distribution. General relations for any stream cross-section are given for the sign and relative size of the integrals. Using the Karman–Prandtl velocity distribution laws for circular pipes the integrals are evaluated numerically and given as functions of the bulk Reynolds number, the pipe friction factor, and other useful quantities likely to be known in practice.

Definitions

The kinetic energy in the fluid which passes a given section of a stream per unit time is

$$E = \int_A \tfrac{1}{2} \rho v^2 u \, da,$$

and the component of the linear momentum normal to the plane of the section is

$$M = \int_A \rho u^2 da,$$

where ρ = mass density of the fluid,

v = velocity at a point on the section,

u = normal component of the velocity,

A = the total area of the section and,

da = the differential area.

In most of the cases where the correction factors can be applied, the stream will be of constant section and the velocity sufficiently close to the purely axial that it may be assumed that $u = v$, in which case

$$E = \int_A \tfrac{1}{2} \rho u^3 da.$$

---

[1] *Manuscript received in original form July 25, 1942, and as revised, October 10, 1942.*
Contribution from the Division of Mechanical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1093.

[2] *Physicist.*

Energy and momentum are usually expressed in terms of the mean velocity $u = \int_A \frac{uda}{A}$ as follows:

$$E = \alpha \tfrac{1}{2} \rho \bar{u}^3 A,$$

and

$$M = \beta \rho \bar{u}^2 A,$$

where α and β are respectively the energy and momentum correction factors. As thus defined these factors are specifically

$$\alpha = \frac{1}{A}\int_A \left(\frac{u}{\bar{u}}\right)^3 da$$

$$\beta = \frac{1}{A}\int_A \left(\frac{u}{\bar{u}}\right)^2 da.$$

The use of these coefficients has been discussed by O'Brien and Johnson (2), who gave some numerical values occurring in practice. The momentum factor may be used in some cases to correct measurements of water flow by the Gibson method (4).

General Relation Between the Coefficients

Let $\frac{u}{\bar{u}} = 1 + z$, and note that by definition $\int_A zda \equiv 0$. On expanding, the factors become

$$\alpha = \frac{1}{A}\int_A (1 + 3z + 3z^2 + z^3)da \equiv 1 + 3I_1 + I_2$$

and

$$\beta = \frac{1}{A}\int_A (1 + 2z + z^2)da \equiv 1 + I_1,$$

where

$$I_1 = \frac{1}{A}\int_A z^2 da \quad \text{and} \quad I_2 = \frac{1}{A}\int_A z^3 da.$$

The only general relation between α and β is thus found to be

$$\alpha - 1 = 3(\beta - 1) + I_2.$$

Since z is a real quantity, z^2 is always positive and therefore I_1 is always positive. I_2 may be either positive or negative, depending on the velocity distribution. In the majority of the practical problems involving flow in pipes, ducts, and channels it will be found that

(a) there are no negative velocities, and

(b) the mean velocity is more than half the maximum velocity,

or, simply, $0 \leqslant u \leqslant 2\bar{u}$. In these cases $|z| \leqslant 1$ and consequently $|z^2| \geqslant |z^3|$, with the result that $|I_1| > |I_2|$. This provides a very useful relation in checking numerical results. It can further be shown that if the velocity distribution is of a certain kind, which is found in most closed ducts and many open channels, the value of I_2 is negative. All the above relations apply to streams with any shape of cross-section.

The Velocity Distribution in Circular Pipes

As a result of the theoretical contributions of Prandtl and von Karman and the experimental work of Nikuradse, it is possible to predict very closely the velocity distribution in circular pipes with fully developed turbulent flow. A résumé of this subject has been presented by Bakhmeteff (1), and the numerical constants quoted by him will be used here.

In a recent instance it was desired to know the value of α for a particular pipe. This was determined experimentally by taking the following steps. A special pitot tube and supporting and traversing apparatus was designed and constructed. Velocity traverses were made on two mutually perpendicular diameters, taking 17 points on each diameter. Assuming that the distribution measured on a radius could be applied with accuracy to the whole quadrant, the values of the α and β were obtained, integrating by the use of a planimeter. After securing the experimental values, the coefficients were computed using Karman–Prandtl universal velocity distributions. The results were as follows:

	α	β
By experiment	1.044	1.013
By Karman–Prandtl formulae	1.043	1.015

This clearly indicated that unless it is possible to undertake experiments of a high order of accuracy, the values of α and β for circular pipes may be computed with entire satisfaction from an assumed velocity distribution.

Additional Notation

In addition to the symbols used above, the following are also required,

u_m = the maximum velocity, occurring at the centre of the pipe,

u_* = the friction velocity $= \sqrt{\frac{\tau}{\rho}}$,

τ = the shear stress in the fluid at the pipe wall,

r = the radius of the pipe,

x = the distance from the pipe wall divided by the radius,

ν = the kinematic viscosity of the fluid,

k = a linear dimension denoting the scale of the roughness,

R_* = the friction Reynolds number $= \frac{u_* r}{\nu}$,

R = the bulk Reynolds number $= \frac{\bar{u}2r}{\nu}$,

λ = the pipe friction factor $= \frac{8\tau}{\rho \bar{u}^2}$,

C_1, C_2, C_3 = numerical constants.

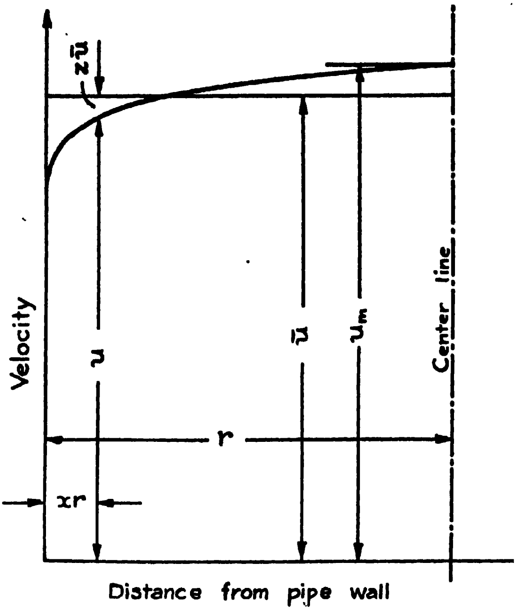


FIG. 1. *Diagram illustrating notation used.*

Derivation of Correction Factors

The dimensionless universal velocity distributions are *(a)* for smooth walled pipes

$$\frac{u}{u_*} = C_1(\ln x + \ln R_* + C_2) \tag{1}$$

and *(b)* for rough walled pipes

$$\frac{u}{u_*} = C_1\left(\ln x + \ln \frac{r}{k} + C_3\right), \tag{2}$$

each of which may be expressed as

$$\frac{u}{u_*} = \frac{u_m}{u_*} + C_1 \ln x\,. \tag{3}$$

When plotted in this form each velocity distribution curve is identical in shape with every other, the only distinguishing feature being the vertical position, denoted by the value of $\frac{u_m}{u_*}$. If, therefore, the vertical position is known the velocity distribution is completely determined and the energy and momentum correction factors can readily be found.

The mean velocity is obtained by integrating over the area of the circle

$$\frac{\bar{u}}{u_*} = 2\int_0^1 \left(C_1 \ln x + \frac{u_m}{u_*}\right)(1 - x)dx = \frac{u_m}{u_*} - \frac{3}{2}\,C_1\,. \tag{4}$$

The variation velocity ratio

$$z = \frac{u}{\bar{u}} - 1 = \frac{C_1 u_*}{u}\left(\ln x + \frac{3}{2}\right)$$

and the integrals occurring in the correction factors become

$$I_1 = \frac{1}{A}\int_A z^2 da = 2\left(\frac{C_1 u_*}{\bar{u}}\right)^2 \int_0^1 \left(\ln x + \frac{3}{2}\right)^2 (1 - x)\,dx = \frac{5}{4}\left(\frac{C_1 u_*}{\bar{u}}\right)^2, \quad (5)$$

and

$$I_2 = \frac{1}{A}\int_A z^3 da = 2\left(\frac{C_1 u_*}{\bar{u}}\right)^3 \int_0^1 \left(\ln x + \frac{3}{2}\right)^3 (1 - x)\,dx = -\frac{9}{4}\left(\frac{C_1 u_*}{\bar{u}}\right)^3. \quad (6)$$

Special Treatment of Low Reynolds Numbers

Since the universal velocity distributions do not apply in the region close to the wall, there seemed some doubt as to the validity of integrating in this region, particularly as the velocities pass through zero and negative values and finally become infinite at the wall. As a check on the magnitude of the error that might arise, a better approximation was made in this region by assuming the laminar distribution. Thus

$$\frac{u}{u_*} = R_*\left(x - \frac{x^2}{2}\right) \qquad \text{for } 0 < x < x_1$$

$$\frac{u}{u_*} = C_1(\ln x + \ln R_* + C_2) \qquad \text{for } x_1 < x < 1,$$

where x_1 is the larger of the two roots of the equation

$$x - \frac{x^2}{2} + \frac{C_1}{R_*}\ln\frac{1}{x} = \frac{C_1}{R_*}(\ln R_* + C_2).$$

This required that all integrations be done in two parts, from 0 to x_1 by one formula and from x_1 to 1 by another. The integrals in the laminar portion become polynomials in the powers of x_1. The process was cumbersome, and was carried out only for four discrete values of R_*. The results of these checks showed that above $R_* = 10{,}000$ the error caused by applying Equation (3) over the whole pipe area is not appreciable.

The comparison between the simple formula and the improved approximation is as follows:

R_*	I_1		I_2	
	Univ. dist.	U.D. + laminar	Univ. dist.	U.D. + laminar
200	0.0347	0.0661	−0.0104	−0.0337
500	0.0261	0.0377	−0.0068	−0.0168
2000	0.0181	0.0207	−0.0039	−0.0065
10000	0.0127	0.0132	−0.0023	−0.0028

Conversion to Convenient Forms

In using Equations (5) and (6) to obtain actual values of α and β it may be that other quantities are more readily known than $\frac{C_1 u_*}{\bar{u}}$ which appears. Below are given a number of convenient substitutions

$$\frac{C_1 u_*}{\bar{u}} = \frac{1}{\left(\ln R_* + C_2 - \frac{3}{2}\right)} \text{ for smooth pipes,}$$

$$= \frac{1}{\left(\ln \frac{r}{k} + C_3 - \frac{3}{2}\right)} \text{ for rough pipes,}$$

$$= C_1 \sqrt{\frac{\lambda}{8}} \text{ for both smooth and rough pipes,}$$

$$= \frac{1}{3}\epsilon, \text{ for both smooth and rough pipes, where } \epsilon = \frac{u_m}{\bar{u}} - 1.$$

(This is a term used by Rehboch (3) in expressions for α and β based on the elementary assumption that the velocity vs. area diagram is a straight line. For Rehboch's case $\alpha = 1 + \epsilon^2$ and $\beta = 1 + \frac{1}{3}\epsilon^2$, whereas for the present case $\alpha = 1 + \frac{5}{3}\epsilon^2 - \frac{2}{3}\epsilon^3$ and $\beta = 1 + \frac{5}{9}\epsilon^2$).

It is expected that for engineering use it will be most convenient to refer the coefficients to R, the bulk Reynolds number, for smooth walled pipes, and to λ, the friction factor, for rough walled pipes. Tables I and II have been prepared in this form and the same results are presented in graphical

TABLE I

FOR SMOOTH WALLED PIPES

$\log_{10} R_*$	$\log_{10} R$	α	β
2.301	3.767	1.164	1.066
2.699	4.234	1.096	1.038
3.301	4.918	1.056	1.021
4.000	5.695	1.037	1.013
4.301	6.025	1.031	1.011
4.699	6.459	1.027	1.009
5.000	6.786	1.024	1.008
5.301	7.111	1.021	1.0075
5.699	7.539	1.019	1.0065
6.000	7.861	1.017	1.006
6.301	8.181	1.016	1.0055
6.699	8.605	1.014	1.005
7.000	8.925	1.013	1.0045

TABLE II

FOR ROUGH WALLED PIPES

λ	α	β	λ	α	β
0.010	1.028	1.010	0.030	1.080	1.029
0.012	1.033	1.012	0.0333	1.088	1.033
0.014	1.038	1.014	0.0367	1.097	1.036
0.016	1.044	1.016	0.04	1.105	1.039
0.018	1.049	1.018	0.045	1.117	1.044
0.020	1.054	1.020	0.05	1.129	1.049
0.0225	1.061	1.022	0.055	1.141	1.054
0.025	1.067	1.024	0.06	1.153	1.059
0.0275	1.073	1.027			

form in Figs. 2 and 3. In all the numerical calculations the following values were given to the constants; $C_1 = 2.5$, $C_2 = 2.2$. The bulk Reynolds number is obtained from the friction Reynolds number by the equation

$$R = 2R_*\left(\ln R_* + C_1C_2 - \frac{3}{2}C_1\right),$$

with appropriate corrections for the low Reynolds numbers.

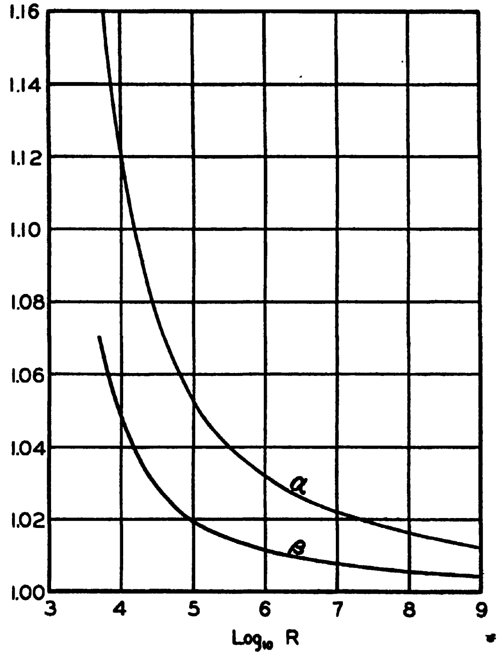


FIG. 2. *Values of α and β against bulk Reynolds number.*

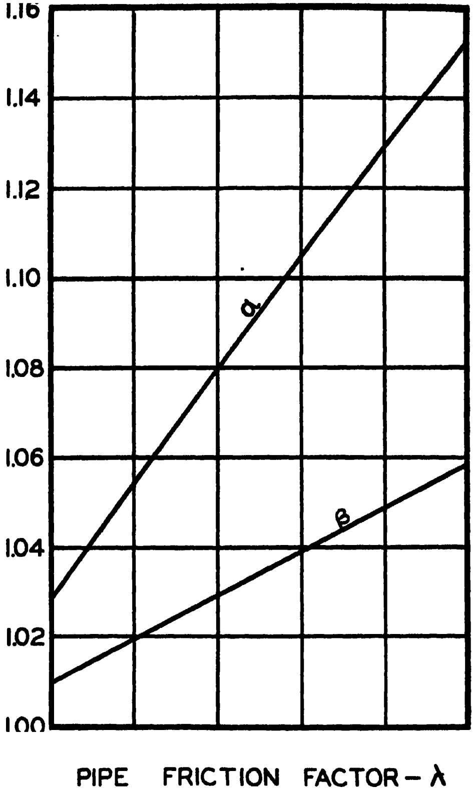


FIG. 3. *Values of α and β against pipe friction factor.*

References

1. BAKHMETEFF, B. A. The mechanics of turbulent flow. Princeton University Press, Princeton, N.J. 1936.
2. O'BRIEN, M. P. and JOHNSON, J. W. Eng. News-Record, 113 : 214-216. 1934.
3. REHBOCH, T. Bauingenieur, vol. 15. 1922.
4. THOMA, D. Mitt. Hydr. Inst. München, No. 1, pp. 59-74. 1926. (English translation in Trans. Am. Soc. Mech. Engrs. 57 : 203-211. 1935.)

SECTION A

INDEX TO VOLUME 20

Authors

Babbitt, J. D.—On the adsorption of water vapour by cellulose, 143.

Brown, W. W.—See Langstroth, G. O.

Buchanan, D.—Second genus crossed orbits, 11.

Charnley, F.—The variances of the means and the variance of the slope of the line of relation of a linear, composite, bivariate distribution, 6.

Coulthard, W. B.—Operational methods of dealing with circuits excited by sinusoidal impulses, 33.

Cullwick, E. G.—The theory of some a-c. commutator motors with series characteristics.
  I. The repulsion motor, 49.
  II. The Winter–Eichberg compensated repulsion motor, 83.
  III. The three-phase series motor, 97.

Douglas, A. E. and Herzberg, G.—Band spectrum and structure of the CH^+ molecule; identification of three interstellar lines, 71.

Dunbar, W. B.—See Young, C. R.

Herzberg, G.—See Douglas, A. E.

Langstroth, G. O. and Brown, W. W.—Absorption phenomena in a condensed spark source, 173.

Langstroth, G. O. and Newbound, K. B.—The influence of sample composition on magnesium, cadmium, and lead intensity ratios as radiated from a spark source, 39.

Newbound, K. B.—See Langstroth, G. O.

Nichols, H. J.—See Wrenshall, G. A.

Ruedy, R.—Absorption of light and heat radiation by small spherical particles. II. Scattering of light by small carbon spheres, 25.

Spinks, J. W. T.—Rotational structure of the Birge–Hopfield bands of N_2, 1.

Tupper, K. F.—Note on the energy and momentum correction factors for flow in circular pipes, 195.

Wrenshall, G. A. and Nichols, H. J.—Secondary radiation from X-ray filters. I. Single-metal filters, 185.

Young, C. R. and Dunbar, W. B.—Lateral support of steel columns and struts, 115.

SECTION A

INDEX TO VOLUME 20

Subjects

Absorption of light and heat radiation by small spherical particles. II. Scattering of light by small carbon spheres, 25.

Absorption phenomena in a condensed spark source, 173.

A-c. commutator motors with series characteristics, The theory of some,
  - I. The repulsion motor, 49.
  - II. The Winter–Eichberg compensated repulsion motor, 83.
  - III. The three-phase series motor, 97.

Adsorption
  - Heat of, of water vapour by cellulose, 152.
  - isotherm for cellulosic materials, 145.
  - of water vapour by cellulose, 143.

Aluminium X-ray filter, Secondary radiation from, 185.

Band spectrum and structure of the CH^+ molecule; identification of three interstellar lines, 71.

Birge–Hopfield bands of N_2, Rotational structure of, 1.

Cadmium, magnesium, and lead intensity ratios as radiated from a spark source, Influence of sample composition on, 39.

Carbon spheres, Small, Scattering of light by, 25.

Cellulose, Adsorption of water vapour by, 143.

CH^+ molecule, Band spectrum and structure of; identification of three interstellar lines, 71.

Circuits excited by sinusoidal impulses, Operational methods of dealing with, 33.

Circular pipes, See Pipes, Circular.

Columns, Steel, and struts, Lateral support of, 115.

Communication engineering, Operational methods of dealing with circuits excited by sinusoidal impulses, 33.

Compensated repulsion motor, Winter–Eichberg, Theory of, 83.

Composite, bivariate distribution, Linear, The variance of the means and the variance of the slope of the line of relation of a, 6.

Condensed spark source, Absorption phenomena in, 173.

Copper X-ray filter, Secondary radiation from, 185.

Crossed orbits, Second genus, 11.

Deslandres table of CH^+ bands, 73.

Dissociation energy of CH^+, 79.

Dissociation of polyatomic molecules by electron impacts, Ionization and, See under Polyatomic molecules.

Distribution, Statistical, See Composite, bivariate distribution.

Electrical current, See Circuits excited by sinusoidal impulses.

Electrical motor(s), Theory of some
  - Repulsion, 49.
  - Three-phase series, 97.
  - Winter–Eichberg compensated repulsion, 83.

Electromotive forces, See Circuits excited by sinusoidal impulses.

Electron impacts, Ionization and dissociation of polyatomic molecules by, See under Polyatomic molecules.

Electrons, Motion of, in "crossed orbit" model of normal helium atom, 11.

Energy and momentum correction factors for flow in circular pipes, Note on, 195.

Filters, X-ray, Secondary radiation from, I. Single-metal filters, 185.

First genus orbits, 11.

Flow in circular pipes, Note on energy and momentum correction factors for, 195.

Heat of adsorption of water vapour by cellulose, 152.

Heat radiation and light, Scattering of, by small spherical particles, 25.

Helium atom, Second genus crossed orbits, 11.

Hydraulics
  Note on energy and momentum correction factors for flow in circular pipes, 195.

Impulses, Sinusoidal, Operational methods of dealing with circuits excited by, 33.

Industrial radiology
  Secondary radiation from X-ray filters. I. Single-metal filters, 185.

Intensity ratios
  of line pairs in spectrum of magnesium, of mercury, and of tin, Dependence of, on amount of element in source, 173.
  Magnesium, cadmium, and lead, as radiated from a spark source, Influence of sample composition on, 39.

Interstellar lines, Band spectrum and structure of the CH^+ molecule; identification of three, 71.

Ionization and dissociation of polyatomic molecules by electron impacts, See under Polyatomic molecules.

Ionization potential of CH, 79.

Lateral support of steel columns and struts, 115.

Lead, magnesium, and cadmium intensity ratios as radiated from a spark source, Influence of sample composition on, 39.

Lead X-ray filter, Secondary radiation from, 185.

Light, Scattering of, by small carbon spheres, 25.

Magnesium
  cadmium, and lead intensity ratios as radiated from a spark source, Influence of sample composition on, 39.
  Intensity ratios of line pairs in spectrum of magnesium, of mercury, and of tin, Dependence of, on amount of element in source, 173.

Medical radiology
  Secondary radiation from X-ray filters. I. Single-metal filters, 185.

Mercury, See under Spectrum.

Molecular constants of CH^+, 76.

Motors, A-c. commutator, with series characteristics, Theory of some, 49, 83, 97.

N_2, Rotational structure of the Birge–Hopfield bands of, 1.

Particles, Small spherical, Absorption of light and heat radiation by, 25.

Pipes, Circular, Note on energy and momentum correction factors for flow in, 195.

Polarization of light scattered by small carbon spheres, 31.

Polyatomic molecules, Ionization and dissociation of, by electron impacts, Bearing of value of ionization potential of CH on, 71.

Radiation, Light and heat, Absorption of, by small spherical particles. II. Scattering of light by small carbon spheres, 25.

Radiation, Secondary, from X-ray filters. I. Single-metal filters, 185.

Radiology
  Secondary radiation from X-ray filters. I. Single-metal filters, 185.

Rectifier, Straight line, Formulae for current flowing in a circuit consisting of a condenser and a loading resistance when fed from a, 33.

Repulsion motor, Theory of, 49.

Rotational constants of CH^+, 75.

Rotational structure of the Birge–Hopfield bands of N_2, 1.

Scattering of light by small carbon spheres, 25.

Secondary radiation from X-ray filters. I. Single-metal filters, 185.

Second genus crossed orbits, 11, 13.

Series motor, Three-phase, Theory of, 97.

Sinusoidal impulses, Circuits excited by, Operational methods of dealing with, 33.

Spark source
  Condensed, Absorption phenomena in, 173.
  Influence of sample composition on magnesium, cadmium, and lead intensity ratios as radiated from a, 39.

Spectrum
  Band, and structure of the CH^+ molecule; identification of three interstellar lines, 71.
  of magnesium, cadmium, and lead, Influence of sample composition on intensity ratios as radiated from a spark source, 39.
  of magnesium, of mercury, and of tin, Intensity ratios of line pairs in, Dependence of, on amount of element in source, 173.

Statistics, See Composite, bivariate distribution.

Steel columns and struts, Lateral support of, 115.

Structural engineering, Lateral support of steel columns and struts, 115.

Structure and band spectrum of the CH^+ molecule; identification of three interstellar lines, 71.

Struts, Steel, and columns, Lateral support of, 115.

Three-phase series motor, Theory of, 97.

Tin, See under Spectrum.

Tin X-ray filter, Secondary radiation from, 185.

Vibrational constants of CH^+, 73.

Water vapour, Adsorption of, by cellulose, 143.

Wave forms, Complex, Method of deducing operational expressions for, 33.

Winter–Eichberg compensated repulsion motor, Theory of, 83.

X-ray filters, Secondary radiation from, I. Single-metal filters, 185.

CANADIAN JOURNAL OF RESEARCH

VOLUME 20
1942
SECTION B

CANADA

Published by the
NATIONAL
RESEARCH COUNCIL
of CANADA

19222

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. JANUARY, 1942 NUMBER 1

LE CALCIUM ET LE MANGANÈSE DANS LES SÈVES ET LES SIROPS D'ÉRABLE[1]

PAR ELPHÈGE BOIS[2], LOUIS-CHARLES DUGAL[3] et MAURICE LESSARD[4]

Résumé

Au cours de la concentration de la sève d'érable en sirop, il y a précipitation des sels de calcium et de manganèse. Dans les sirops à 63% de solides il y a deux fois plus de CaO que dans ceux à 67%. Dans un évaporateur en aluminium, au moins 75% du manganèse est précipité. C'est là une des causes qui font varier les indices analytiques des sirops filtrés.

Introduction

La sève d'érable contient du sucrose et aussi des sels (6, 7). Au cours de la fabrication du sirop, la concentration dans l'évaporateur provoque la précipitation d'une partie de ces sels. Ceux qui restent dans le sirop filtré ont servi de base à une méthode d'analyse pour reconnaître la falsification des produits de l'érable. Cette méthode procède soit par la mesure de la conductivité électrique du sirop dilué, soit encore par la calcination du sirop et les déterminations des cendres totales, solubles et insolubles, aussi l'alcalinité de ces cendres. Les valeurs ainsi obtenues doivent être comprises entre certaines limites qui ont été fixées par l'analyse d'un grand nombre de sirops de pureté reconnue (3, 9, 10, 11).

Signalons que Delorme (5), Riou et Delorme (8) ont proposé un indice de manganèse.

Nous considérerons la teneur en calcium et en manganèse des sèves et des sirops d'érable, ce qui permettra d'expliquer, en partie du moins, la variation des valeurs limites ou indices analytiques des *sirops filtrés*.

Partie expérimentale

La minéralisation

Pour la détermination de ces éléments, il est nécessaire de détruire la matière organique. Les résultats obtenus par la calcination varient suivant des causes insuffisamment déterminées: la température plus ou moins élevée atteinte durant l'opération et la formation de composés plus ou moins solu-

---

[1] *Manuscrit original reçu le 24 mars 1941, et sous forme revisée le 17 novembre 1941.*
Contribution du Laboratoire de Biochimie, Faculté des Sciences, Université Laval, Québec Qué.

[2] *Professeur de biochimie à l'Université Laval.*

[3] *Étudiant gradué, Université Laval.*

[4] *Chimiste au Ministère provincial de l'Agriculture, Québec.*

bles. La minéralisation par voie humide élimine ces causes. Elle est employée avec succès dans nombre d'analyses biochimiques (2, 4).

Nous avons choisi celle par l'acide nitrique en présence de l'acide sulfurique (1, p. 371); sa conduite est facile avec les sirops et les risques d'accidents sont minimes. Après la destruction de la matière organique (nous prenons une quantité de sève ou de sirop contenant 20 g. de matière solide, d'après l'indice de réfraction), le liquide est porté à 500 ml. et les déterminations des différents éléments se poursuivent sur des aliquots.

Le calcium

Nous avons prélevé 50 ml. de la solution et précipité le calcium sous forme d'oxalate (1, p. 347). Ce dernier a été dosé par une solution *N*/50 de permanganate de potassium. Les résultats sont donnés en pourcentage de CaO par rapport à la matière solide. Voir le Tableau I.

TABLEAU I

LE CALCIUM DANS LES SÈVES ET LES SIROPS D'ÉRABLE

Échantillons	Solides, %	CaO, % de solides
Mélange *A*, sèves *S.E.P.* 1938		0.413
Mélange *B*, sèves *S.E.P.* 1938		0.418
Mélange *C*, sèves *S.E.P.* 1938		0.418
Mélange *A*, sèves *S.E.P.* 1939		0.350
Mélange *B*, sèves *S.E.P.* 1939		0.388
Mélange *C*, sèves *S.E.P.* 1939		0.449
Mélange *A*, sèves *S.E.P.* 1940		0.540
Mélange *B*, sèves *S.E.P.* 1940		0.602
N° 126, sirop *S.E.P.* 1940	63.3	0.502
N° 108, sirop *S.E.P.* 1940	63.8	0.530
N° 115, sirop *S.E.P.* 1940	65.9	0.400
N° 119, sirop *S.E.P.* 1940	67.0	0.221
N° 112, sirop *S.E.P.* 1940	67.0	0.185
N° 123, sirop *S.E.P.* 1940	67.2	0.196
Sirop *M* 1940	66.0	0.115
Sirop *N* 1940	67.2	0.118

Le manganèse

Les déterminations du manganèse furent faites suivant la méthode au persulfate (1, p. 521). Les résultats sont exprimés en parties de manganèse par million de parties de matière solide dans l'échantillon. Voir le Tableau II.

Commentaires et conclusions

Les sèves provenaient de la Station expérimentale de Plessisville, P.Q. Leur teneur en calcium et en manganèse varie sensiblement au cours de la même saison et davantage d'une saison à l'autre. Les sirops *S.E.P.* furent

TABLEAU II

LE MANGANÈSE DANS LES SÈVES ET LES SIROPS D'ÉRABLE

Échantillons	Solides, %	Mn, p.p.m. de solides
Mélange *A*, sèves *S.E.P.* 1940	2.4	22.0
Mélange *B*, sèves *S.E.P.* 1940	2.6	20.0
Mélange *C*, sèves *S.E.P.* 1940	3.1	33.0
N° 110, sirop *S.E.P.* 1940	62·3	1·0
N° 126, sirop *S.E.P.* 1940	63.3	4.3
N° 108, sirop *S.E.P.* 1940	63.8	3.5
N° 112, sirop *S.E.P.* 1940	67.0	1.5
N° 123, sirop *S.E.P.* 1940	67.2	4.0
Sirop *M* 1940	66.0	70.0
Sirop *N* 1940	67.2	63.0

préparés au même endroit dans des ustensiles en aluminium: chalumeaux, chaudières à sève, réservoirs et évaporateur. Les sirops *M* et *N* provenaient d'une érablière voisine munie d'appareils en fer-blanc. Tous les sirops ont été filtrés sur feutre. On constate que le pourcentage de CaO diminue à mesure qu'augmente la concentration des sirops. C'est à 65% de solides environ que la variation dans la concentration du sirop affecte le plus la quantité de CaO. Il y a deux fois plus de CaO dans les sirops à 63% que dans ceux à 67%. Il est à remarquer que la teneur en calcium n'est pas constante pour une concentration donnée du sirop; les sirops à 67.0% et 67.2% de solides en sont des exemples. Nous avons constaté en outre que l'ébullition du sirop d'érable filtré provoque une nouvelle précipitation. La gradation observée pour le calcium ne s'est pas répétée pour le manganèse.

Nous soulignons que Delorme (5, p. 33) a déterminé l'indice de manganèse des sèves de St-Vincent-de-Paul et qu'il a trouvé des valeurs identiques aux nôtres pour les sèves de Plessisville: 20 à 30 p.p.m. (2.0 à 3.0 mg. pour 100 g. de M.S.).

Ces indices, inféreurs à 5, sont ceux de la sève d'érable, le plus pur des produits de l'érable. Les sirops qui ont un indice plus élevé seraient contaminés par le manganèse des ustensiles, comme nos sirops *M* et *N*.

Cette précipitation et cette contamination irrégulière sont au nombre des facteurs qui font varier le pourcentage des cendres, l'alcalinité des cendres, la conductivité électrique, et d'autres indices analytiques des sirops.

Présentement, les déterminations du manganèse ne permettent pas plus que celles du calcium de fixer des limites pour déceler la falsification des produits de l'érable qui ont été *filtrés*.

Bibliographie

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 4th ed. A.O.A.C., Washington, D.C. 1935.
2. Bartholomew, R. J. Analyst, 63 : 884-886. 1938.
3. Bryan, A. H. U. S. Dept. Agr. Bull. 134. 1910.
4. Buell, M. V. J. Biol. Chem. 130 (1) : 357-363. 1939.
5. Delorme, J. Rev. Oka, 11 : 3-13, 30-40. 1937.
6. Jones, C. H. Vermont Agr. Expt. Sta. 18th Ann. Rept., pp. 315-339. 1905.
7. Jones, C. H. et Hollister, F. M. Vermont Agr. Expt. Sta. 17th Ann. Rept., pp. 457-461. 1904.
8. Riou, P. et Delorme, J. Can. J. Research, B, 19 : 68-72. 1941.
9. Snell, J. F. Ind. Eng. Chem. 5 (9) : 740-747. 1913.
10. Snell, J. F. Trans. Roy. Soc. Can. (Ser. 3) 13 (Sec. 3) : 221-231. 1919.
11. Snell, J. F. et Scott, J. M. Ind. Eng. Chem. 5 (12) : 993-997. 1913.

CHEMOTHERAPEUTIC STUDIES: PREPARATION OF SUBSTITUTED SULPHONAMIDES[1]

By C. Marchant[2], C. C. Lucas[3], and L. McClelland[2]

WITH AN APPENDIX

THE DETERMINATION OF CHEMOTHERAPEUTIC ACTIVITY

By P. H. Greey[4]

Abstract

A series of substituted sulphonamides has been prepared for a study of their chemotherapeutic activity against a number of different bacterial species. By condensing *p*-acetylaminobenzenesulphonyl chloride with primary aromatic and aliphatic amines, N^4-acetyl-N^1-substituted sulphanilamides were obtained. Hydrolysis with acid or alkali removed the acetyl group and gave the desired N^1-substituted sulphanilamides.

The appendix contains details of the techniques used in testing these sulphonamides. Although a few of the compounds described in this paper exhibit considerable *in vitro* activity, none of them possess, *in vivo*, chemotherapeutic properties equal to those of sulfapyridine or sulfathiazole.

Introduction

Late in 1937 this laboratory became interested in the biochemical, clinical, and experimental aspects of the chemotherapy of bacterial infections. The results of these studies (5, 7, 8, 9) so stimulated the writers' interest that a program of synthesis was embarked upon, in the hope of finding drugs with specific activity towards staphylococci, *M. tuberculosis*, or other species not controlled by sulphanilamide.

Since the latter part of 1938 a large number of new sulphonamides have been prepared by the writers and tested by Dr. P. H. Greey, of the Department of Pathology and Bacteriology, against many different bacterial species *in vitro* and against *Streptococcus haemolyticus*, *Pneumococcus*, and *Staphylococcus in vivo;* furthermore, the curative power of some was tested with guinea pigs infected with *M. tuberculosis*. Several of these derivatives were fairly active against streptococci, but they were not as good as sulphanilyl α-amino pyridine (*M* and *B* 693, dagenan, sulfapyridine). Although no new drug with particularly desirable antibacterial characteristics has been found, it seems advisable to put on record some of the substances studied to date. A few of the compounds prepared and tested here have, in the meantime, been examined in other laboratories and are now recorded in the literature; the writers have learned that certain others have been studied elsewhere, but the findings have never been published.

---

[1] *Manuscript received August 28, 1941.*

Contribution from the Department of Medical Research, Banting Institute, University of Toronto, Toronto, Ont.

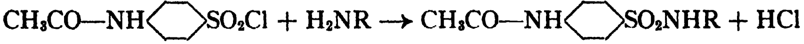
[2] *Research Assistant.*

[3] *Associate Professor.*

[4] *Lecturer in Bacteriology, Department of Pathology and Bacteriology, University of Toronto; Bacteriologist to the Toronto General Hospital.*

The accompanying list of compounds is submitted in the hope that others may also record compounds tested and found to be unsuitable, since only in this way can unnecessary duplication of effort be avoided. The writers know of one case in which at least five different laboratories studied the same compound, but none of them published their negative findings. More rapid advances could undoubtedly be made if the present wasteful replication of work could be eliminated.

The substituted sulphanilamides listed in this publication were prepared by condensing *p*-acetylaminobenzenesulphonyl chloride with an amine (see equation)



either by gently warming equimolecular quantities of the reactants in acetone solution in the presence of pyridine (Method I), or by melting an intimate mixture of one mole of the acid chloride with two moles of the amine (Method II). The product of the reaction in acetone was precipitated by the addition of four volumes of cold water. This impure material, or the product obtained by the fusion procedure, was purified by dissolving in a minimum quantity of cold dilute sodium hydroxide solution, extracting with ether to remove impurities, precipitating from the alkaline solution with dilute hydrochloric acid, and recrystallizing from a suitable solvent. The yields of the pure compounds ranged from 50 to 95%, but were usually more than 70%. Some properties of the compounds so obtained are shown in Table I. Attempts to condense arsanilic acid with *p*-acetylaminobenzenesulphonyl chloride were completely unsuccessful. N^4-acetyl-N^1-(4-arsonophenyl)-sulphanilamide was finally obtained by the Bart reaction (1) from N^4-acetyl-N^1-(4-aminophenyl)-sulphanilamide.

To remove the acetyl radical protecting the amino group, the compounds were hydrolysed by refluxing with either hydrochloric acid or sodium hydroxide solution. The product of the acid hydrolysis, which usually separated out on cooling, was recrystallized from aqueous ethyl alcohol or other suitable solvent. When alkaline hydrolysis was employed the product was obtained by neutralizing to litmus, filtering, and recrystallizing. The yields, based on the acetyl derivative taken, were between 50 and 90%. The compounds so prepared are listed in Table II.

Compounds containing a nitro group were usually converted to the corresponding amino compound by catalytic reduction. Theoretical amounts of hydrogen were taken up, but, owing to losses in purification, the final yield of pure product was usually only 50 to 75% of that expected from the nitro compound. In a few cases, reduction with ferrous hydroxide was used.

The carbethoxy compounds were made in the usual way by esterifying the acids with absolute ethyl alcohol in the presence of hydrogen chloride. The acids with carboxyl groups para or meta to the sulphonamide linkage esterified readily, but the ortho compound gave only low yields even with much longer refluxing. These compounds are listed in Table II.

TABLE I

N^4-ACETYL-N^1-SUBSTITUTED SULPHANILAMIDES

N^4-Acetyl-N^1-substituted sulphanilamide	M.p.° C.†	Method of prepn.	Crystal form	Recrystallized from
N^1-(4-nitrophenyl) (2, 11)	258	I, II	Light yellow rods	95% Alcohol
N^1-(3-nitrophenyl) (11)	244	I	Light yellow prisms	50% Alcohol
N^1-(2-nitrophenyl) (11)	200	II	Yellow prisms	95% Alcohol
N^1-(6-methyl-3-nitrophenyl)	266.5	I	Light yellow plates	50% Acetone
N^1-(4-methyl-3-nitrophenyl)	239	I	Light yellow needles	95% Alcohol
N^1-(6-methoxy-3-nitrophenyl)	261.5 dec.	I	Light yellow plates	1 *M* Sodium carbonate
N^1-(4-methoxy-2-nitrophenyl)	175	I	Light yellow rods	50% Alcohol
N^1-(4-aminophenyl)	235		Colourless needles	50% Alcohol
N^1-(4-methylphenyl)	208	I	Colourless hexagonal rods	95% Alcohol
N^1-(3-methylphenyl)	205	I	Colourless pyramids	50% Alcohol
N^1-(2-methylphenyl)	244.5	I	Colourless prisms	95% Alcohol
N^1-(4-methoxyphenyl)	200	I, II	Colourless plates	95% Alcohol
N^1-(3-methoxyphenyl)	193	I	Colourless pyramids	95% Alcohol
N^1-(2-methoxyphenyl)	212	I	Colourless plates	95% Alcohol
N^1-(4-carboxyphenyl)* (2, 6)		I	——	——
N^1-(3-carboxyphenyl) (6)	274	I	Colourless rods	50% Alcohol
N^1-(2-carboxyphenyl) (6)	233	I	Colourless plates	75% Alcohol
N^1-(2, 6-dimethylphenyl)	236.5	I	Colourless flat rods	95% Alcohol
N^1-(2, 4-dimethylphenyl)	214.5	I	Colourless needles	95% Alcohol
N^1-(2-methoxy-5-methylphenyl)	206	II	Colourless rods	95% Alcohol
N^1-(2-methyl-5-isopropylphenyl)	160.5	I	Colourless prisms	95% Alcohol
N^1-(4-acetylphenyl)	254.5	I	Colourless plates	95% Alcohol
N^1-(4-benzoylphenyl)	218.5	I	Colourless rods	95% Alcohol
N^1-(4-bromophenyl)	208	I	Colourless rods	95% Alcohol
N^1-(3-hydroxyethyl) (2)	150	II	Colourless plates	Water
N^1-(4-arsonophenyl)	275 dec.		Colourless rods	30% Alcohol
bis-(acetyl-sulphanilyl)-*p*-phenylene-diamine	316.5 dec.	I	Colourless plates	1 *M* Sodium carbonate
bis-(acetyl-sulphanilyl)-*m*-toluylene-diamine	278	I	Colourless rods	95% Alcohol
bis-(acetyl-sulphanilyl)-benzidine	288	I	Colourless rods	Glacial acetic

* *Prepared but not isolated as pure chemical.*

† *All melting points are corrected.*

Most of these compounds were analysed, but, since the de-acetylated forms derived from them were of correct composition (Table II), the analytical data are not given here.

The method of testing the chemotherapeutic activity of the compounds listed in Table II is briefly described by Dr. Greey in an appendix to this paper. The intermediate compounds shown in Table I were not tested, since many workers (3) have shown that the N^4-substituted derivatives of compounds known to be active possess a greatly diminished activity.

Experimental

p-Acetylaminobenzenesulphonyl chloride. A modification of the method described by Stewart (10) was used to prepare this compound. To 466 gm. (4 moles) of technical chlorosulphonic acid was added 135 gm. (1 mole) of acetanilide, in small portions, with vigorous stirring, care being taken that the temperature did not rise above 70° C. The resulting solution was main-

TABLE II

N^1-SUBSTITUTED SULPHANILAMIDES

Ref. No.	N^1-substituted sulphanilamide	Formula	M.p.°C. †	N %††		Crystal form	Recrystallized from
				Calc.	Found		
1	N^1-(4-nitrophenyl) (2, 11)	$C_{12}H_{11}N_3O_4S$	165	—	—	Light yellow rods	95% Alcohol
2	N^1-(3-nitrophenyl) (11)	$C_{12}H_{11}N_3O_4S$	169	—	—	Yellow rods	50% Alcohol
3	N^1-(2-nitrophenyl)	$C_{12}H_{11}N_3O_4S$	179	—	—	Yellow rods	50% Alcohol
4	N^1-(6-methyl-3-nitrophenyl)	$C_{13}H_{13}N_3O_4S$	199	—	—	Yellow rods	95% Alcohol
5	N^1-(4-methyl-3-nitrophenyl)	$C_{13}H_{13}N_3O_4S$	189	—	—	Light yellow rods	95% Alcohol
6	N^1-(6-methoxy-3-nitrophenyl)	$C_{13}H_{13}N_3O_5S$	188	—	—	Yellow plates	95% Alcohol
7	N^1-(4-methoxy-2-nitrophenyl)	$C_{13}H_{13}N_3O_5S$	117	—	—	Yellow rods	95% Alcohol
8	N^1-(4-aminophenyl) (2, 11)	$C_{12}H_{13}N_3O_2S$	138	15.95	15.75	Colourless needles	25% Alcohol
9	N^1-(3-aminophenyl) (11)	$C_{12}H_{13}N_3O_2S$	177	15.95	15.97	Colourless plates	50% Alcohol
10	N^1-(2-aminophenyl) (11)	$C_{12}H_{13}N_3O_2S$	208	15.95	16.00	Colourless needles	95% Alcohol
11	N^1-(6-methyl-3-aminophenyl)	$C_{13}H_{15}N_3O_2S$	208.5	15.16	15.06	Colourless plates	75% Alcohol
12	N^1-(4-methyl-3-aminophenyl)	$C_{13}H_{15}N_3O_2S$	185	15.16	15.17	Colourless plates	50% Alcohol
13	N^1-(6-methoxy-3-aminophenyl)	$C_{13}H_{15}N_3O_3S$	232	14.32	14.13	Colourless plates	70% Alcohol
14	N^1 (4-methoxy-2-aminophenyl)	$C_{13}H_{15}N_3O_3S$	195	14.32	14.43	Colourless needles	60% Alcohol
15	N^1-(4-methylphenyl)	$C_{13}H_{14}N_2O_2S$	190	10.68	10.32	Colourless rods	95% Alcohol
16	N^1-(3-methylphenyl)	$C_{13}H_{14}N_2O_2S$	133.5	10.68	10.45	Colourless rods	50% Alcohol
17	N^1-(2-methylphenyl)	$C_{13}H_{14}N_2O_2S$	155.5	10.68	10.73	Colourless flat rods	95% Alcohol
18	N^1-(4-methoxyphenyl)	$C_{13}H_{14}N_2O_3S$	194	10.06	9.97	Colourless rods	95% Alcohol
19	N^1-(3-methoxyphenyl)	$C_{13}H_{14}N_2O_3S$	163.5	10.06	10.10	Colourless rods	95% Alcohol
20	N^1-(2-methoxyphenyl)	$C_{13}H_{14}N_2O_3S$	199	10.06	9.94	Colourless prisms	50% Alcohol
21	N^1-(4-carboxyphenyl) (2, 4, 6)	$C_{13}H_{12}N_2O_4S$	197	9.62	9.61	Colourless rods	Water
22	N^1-(3-carboxyphenyl) (6)	$C_{13}H_{12}N_2O_4S$	196	9.62	9.49	Colourless plates	40% Alcohol
23	N^1-(2-carboxyphenyl) (4, 6)	$C_{13}H_{12}N_2O_4S$	226	9.62	9.56	Colourless rods	75% Alcohol
24	N^1-(4-carbethoxyphenyl)	$C_{15}H_{16}N_2O_4S$	230	8.75	8.66	Colourless plates	30% Alcohol
25	N^1-(3-carbethoxyphenyl)	$C_{15}H_{16}N_2O_4S$	105	8.75	8.68	Colourless rods	95% Alcohol
26	N^1-(2-carbethoxyphenyl)	$C_{15}H_{16}N_2O_4S$	165.5	8.75	8.79	Colourless rods	30% Alcohol
27	N^1-(2, 6-dimethylphenyl)	$C_{14}H_{16}N_2O_2S$	231	10.13	10.15	Colourless needles	95% Alcohol
28	N^1-(2, 4-dimethylphenyl)	$C_{14}H_{16}N_2O_2S$	149	10.13	10.18	Colourless rods	80% Alcohol
29	N^1-(2-methoxy-5-methylphenyl)	$C_{14}H_{16}N_2O_3S$	161	9.58	9.56	Colourless plates	50% Alcohol
30	N^1-(2-methyl-5-isopropylphenyl)	$C_{16}H_{20}N_2O_2S$	150.5	9.19	9.10	Colourless plates	50% Alcohol
31	N^1-(4-acetylphenyl)	$C_{14}H_{14}N_2O_3S$	211	9.65	9.68	Colourless rods	95% Alcohol
32	N^1-(4-benzoylphenyl)	$C_{19}H_{16}N_2O_3S$	181.5	7.95	7.94	Colourless needles	95% Alcohol
33	N_1-(4-bromophenyl)	$C_{12}H_{11}N_2O_2SBr$	178	8.56	8.58	Colourless plates	95% Alcohol
34	N^1-β-hydroxyethyl (2)	$C_8H_{12}N_2O_3S$	100	12.95	12.94	Colourless plates	Water
35	N^1-(4-arsonophenyl)*	$C_{12}H_{13}N_2O_5SAs$	**	7.53	7.50	Colourless rods	Water
36	bis-(sulphanilyl)-*p*-phenylenediamine	$C_{18}H_{18}N_4O_4S_2$	263 dec.	13.39	13.51	Colourless plates	1 *M* Sodium carbonate
37	bis-(sulphanilyl)-*m*-toluylenediamine	$C_{19}H_{20}N_4O_4S_2$	229	12.95	12.94	Colourless needles	95% Alcohol
38	bis-(sulphanilyl)-benzidine	$C_{24}H_{22}N_4O_4S_2$	293	11.33	11.28	Colourless plates	1 *M* Sodium carbonate

* *% As. calc. 20.14, found 20.27.*

† *All melting points are corrected.*

** *Chars between 241° C. and 250° C.*

†† *Determined by Kjeldahl method.*

tained at 60° to 65° C. for two hours then poured slowly with vigorous stirring on to 1 kg. of crushed ice. The next steps were carried out in quick succession, since the compound hydrolyses somewhat readily while moist with the acid mother liquor. The precipitate was filtered with suction, washed with 200 cc. of cold water, and partly dried by suction. The paste so obtained was dissolved in about 500 cc. of acetone and precipitated by the addition of two to three litres of cold water, filtered off with suction, and dried in the air. This product (yield, 130 to 140 gm., i.e., 55 to 60%), m.p. above 140° C*., was sufficiently pure to be used in the preparations described below. When kept dry it remained relatively stable for more than a month. Partly decomposed material could be purified by reprecipitation from acetone with water.

Preparation of N^4-Acetyl-N^1-substituted Sulphanilamides

Method I

This method, which involves the use of pyridine as condensing agent, has been described previously by Bauer (2), but none of the preparations given below were reported by him.

N^4-Acetyl-N^1-(4-methoxyphenyl)-sulphanilamide. A solution of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride, 12.3 gm. (0.1 mole) of *p*-anisidine and 12 cc. (about 0.15 mole) of technical pyridine in 80 cc. of acetone was brought just to the boil and allowed to cool to room temperature by standing for two hours. The product, after precipitating by adding about 350 cc. of cold water and filtering, was dissolved in a minimum quantity of 5 *N* sodium hydroxide solution. The solution was diluted with water to about three times the volume, shaken with an equal volume of ether to remove any pyridine and unused amine, and the product was precipitated with dilute hydrochloric acid. The resulting material was dissolved in hot 95% ethyl alcohol, decolorized with charcoal, and allowed to crystallize. On recrystallizing again, 21.4 gm. (70% yield) of the pure compound was obtained as colourless plates, m.p. 200° C. When prepared by Method II, the yield was 24.5 gm. (80%).

N^4-Acetyl-N^1-(6-methoxy-3-nitrophenyl)-sulphanilamide. A solution of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride, 16.8 gm. (0.1 mole) of 6-methoxy-3-nitro-aniline and 12 cc. (about 0.15 mole) of technical pyridine in 80 cc. of acetone was brought just to the boil and allowed to cool to room temperature by standing for two hours. The product was precipitated by adding about 350 cc. of cold water and purified as described above, except that it was recrystallized from a 1 *M* solution of sodium carbonate. The compound was obtained as light yellow plates, m.p. 261.5° C., dec. Yield, 27.5 gm. (75%).

N^4-Acetyl-N^1-(4-methyl-3-acetylsulphanilamido-phenyl)-sulphanilamide.† A solution of 46.8 gm. (0.2 mole) of *p*-acetylaminobenzenesulphonyl chloride, 12.4 gm. of *m*-toluylenediamine, 24 cc. (about 0.3 mole) of technical pyridine in 160 cc. of acetone was brought just to the boil and allowed to cool to room temperature by standing for two hours. The product was precipitated by

---

* *The pure product, recrystallized from benzene, melted at 149° C.*
All melting points are corrected.

† *A shorter name is used in Table I for this compound, viz., bis-(acetylsulphanilyl) m-toluylenediamine.*

adding 350 cc. of cold water and purified by recrystallization from 95% ethyl alcohol; yield, 28 gm. (60%), as colourless rods, m.p. 278° C.

N⁴-Acetyl-N¹-(4-carboxyphenyl)-sulphanilamide. A solution of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride, 13.7 gm. (0.1 mole) of *p*-aminobenzoic acid, and 12 cc. (about 0.15 mole) of technical pyridine in 80 cc. of acetone was brought just to the boil and allowed to cool. After two hours the product was precipitated by adding 350 cc. of cold water. The filtered material was washed with 100 cc. of warm 5 *N* hydrochloric acid to remove any pyridine and unused amine. The insoluble remainder was dissolved in a minimum volume of hot 5 *N* sodium hydroxide solution and cooled. The sodium salt of the compound, which precipitated, was dissolved in hot 50% ethyl alcohol, decolorized with charcoal, and allowed to crystallize. The free acid was obtained by dissolving the sodium salt in water and precipitating with dilute hydrochloric acid. The pure compound was obtained from 30% ethyl alcohol as colourless plates, m.p. 253° C., yield, 22.0 gm. (66%).

Method II

This method, involving fusion of the reactants, gives good yields only when the fusion temperature is not too high and when the fusion mass is not too viscous.

N⁴-Acetyl-N¹-(2-methoxy-5-methylphenyl)-sulphanilamide. An intimate mixture of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride and 27.4 gm. (0.2 mole) of 2-methoxy-5-methylaniline was melted on a water-bath with vigorous stirring, and heated until solid. The product was isolated by dissolving in a minimum quantity of 5 *N* sodium hydroxide solution, diluting with water to three times the volume, and shaking with an equal volume of ether to remove the excess amine, then precipitating with dilute hydrochloric acid. The resulting material was purified by dissolving in hot 95% ethyl alcohol, decolorizing with charcoal, and allowing to crystallize. On recrystallization, 21.7 gm. (65% yield) of colourless rods (m.p. 206° C.) was obtained.

N⁴-Acetyl-N¹-(2-nitrophenyl)-sulphanilamide. An intimate mixture of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride and 27.6 gm. (0.2 mole) of *o*-nitraniline was melted on a water-bath to a liquid and stirred vigorously until almost solid. The product was purified as described above. A yield of 20.0 gm. (60%), as bright yellow prisms (m.p. 200° C.), was obtained. Attempts to prepare this by Method I were not successful.

N⁴-Acetyl-N¹-β-hydroxyethyl-sulphanilamide. A solution of 23.4 gm. (0.1 mole) of *p*-acetylaminobenzenesulphonyl chloride in 12.1 gm. (0.2 mole) of ethanolamine was warmed on a water-bath for one hour. After cooling, the precipitated material was filtered off and recrystallized twice from water, being decolorized with charcoal the first time. The compound was obtained as colourless plates (m.p. 150° C.) in 90% yield (23.3 gm.).

Removal of the N^4-Acetyl Group

Both acid and alkali have been used to hydrolyse these compounds. Since the acetylated compounds are usually insoluble in the acid, the early stages of hydrolysis were accompanied by frothing and bumping. To avoid this, in all later work alkaline hydrolysis was employed, since the sodium salt of these compounds is water-soluble.

Acid Hydrolysis

N^1-(4-Methoxyphenyl)-sulphanilamide. This compound was obtained by refluxing 32.0 gm. (0.1 mole) of N^4-acetyl-N^1-(4-methoxyphenyl)-sulphanilamide with 160 cc. of 5 *N* hydrochloric acid until completely dissolved. This required one hour. On cooling, the hydrochloride of the compound precipitated. Recrystallization from 95% ethyl alcohol gave the free amine. On recrystallizing once more, 22.0 gm. (80% yield based on the acetylated compound) of colourless rods (m.p. 194° C.) was obtained.

Alkaline Hydrolysis

Bis-sulphanilyl-m-toluylene-diamine. A solution of bis-acetylsulphanilyl-*m*-toluylene-diamine in 125 cc. of 2 *N* sodium hydroxide* solution was refluxed for one hour. After cooling, the reaction product was precipitated by neutralizing to litmus with dilute hydrochloric acid and recrystallized twice from 95% ethyl alcohol; colourless needles, m.p. 229° C. Yield, 30.0 gm. (70%, based on acetylated compound).

Reduction of Nitro Group to Amino Group

N^1-(6-Methoxy-3-aminophenyl)-sulphanilamide. A suspension of 3.2 gm. (0.01 mole) of N^1-(6-methoxy-3-nitrophenyl)-sulphanilamide in 30 cc. of 95% ethyl alcohol was shaken with palladium black in an atmosphere of hydrogen at room temperature and atmospheric pressure; the theoretical volume of hydrogen was taken up over a period of three hours. The colour of the suspension changed from yellow to colourless. The amine was dissolved in the alcohol by warming, the palladium filtered off, and the product crystallized from the hot filtrate suitably diluted with water. The amine, which discolours very readily when exposed to air, was dissolved in 70% ethyl alcohol; the solution was treated with charcoal and filtered, and the amine allowed to crystallize. After this operation had been repeated, the yield of pure compound as colourless plates (m.p. 232° C.), was 1.1 gm. (52%). The fact that the theoretical quantity of hydrogen was taken up suggested that the losses occurred during purification. By converting the amine to the hydrochloride and dissolving in hot water, the colour was removed more readily with charcoal and the yield could be increased to 90%. The greater stability of the hydrochloride is a further advantage of this procedure.

---

* *When a carboxy- or arsono-substituted compound was hydrolysed sufficient additional sodium hydroxide was used in order to form the sodium salt.*

N^1-(2-Aminophenyl)-sulphanilamide. A solution of 3.1 gm. (0.01 mole) of the sodium salt of N^1-(2-nitrophenyl)-sulphanilamide in water was stirred vigorously for 15 min. with a suspension of ferrous hydroxide prepared by dissolving 20 gm. of technical ferrous sulphate in 50 cc. of water and making alkaline with about 90 cc. of 2 *N* sodium hydroxide solution. The mixture was filtered through a large suction filter and the ferric hydroxide extracted twice with about 50 cc. of water. The crude product was obtained from the combined washings and filtrate by acidifying with acetic acid and filtering. The yield after decolorizing and recrystallizing from 95% ethyl alcohol was 1.8 gm. (70%). This method has been used by Webster and Powers (11).

Esterification of Carboxyl Groups

N^1-(4-Carbethoxyphenyl)-sulphanilamide. To a solution of 2.92 gm. (0.01 mole) of N^1-(4-carboxyphenyl)-sulphanilamide in 25 cc. of absolute alcohol was added 15 cc. of absolute alcohol saturated with dry hydrogen chloride at 0° C. The solution was refluxed for six hours and then cooled; 400 cc. of 0.5 *M* sodium carbonate solution was cautiously added, the mixture was filtered with suction, and the product recrystallized from 50% alcohol. Colourless plates, m.p. 235° C., were obtained in a yield of 2.7 gm. (82%).

Introduction of Arsono Group

This is an application of the Bart reaction (1).

N^4-Acetyl-N^1-(4-arsonophenyl)-sulphanilamide. A fine suspension of the hydrochloride of N^4-acetyl-N^1-(4-aminophenyl)-sulphanilamide* was made by dissolving 30.5 gm. (0.1 mole) in 60 cc. of hot concentrated hydrochloric acid and quickly adding 100 gm. of crushed ice. The diazonium salt was prepared from this by adding 8 gm. of sodium nitrite in 20 cc. of water and stirring for one-half hour until a creamy precipitate remained. The diazonium mixture was made just alkaline to Congo red by addition of sodium hydroxide solution. To this was added 23.5 gm. of arsenious oxide dissolved in 240 cc. of 2 *N* sodium hydroxide solution and a little copper powder as a catalyst. After stirring vigorously at room temperature for two hours no more nitrogen was evolved and the precipitate was completely dissolved. A brown gummy precipitate that formed on neutralization (litmus) was discarded. The addition of more acid and gentle warming removed the last of the gummy material. On cooling, a colourless crystalline precipitate was formed. Recrystallization from 30% ethyl alcohol gave colourless rods (m.p. 275° C., dec.) in 50% yield (20.5 gm.).

Acknowledgment

This work was supported by a grant from the Banting Research Foundation to whom grateful acknowledgment is made.

---

* *Prepared by catalytic reduction of N^4-acetyl-N^1-(4-nitrophenyl)-sulphanilamide.*

References

1. BART, H. Ann. 429 : 55-103. 1922.
2. BAUER, H. J. Am. Chem. Soc. 61 (3) : 613-616. 1939.
3. BUTTLE, G. A. H., GRAY, W. H., and STEPHENSON, D. Lancet, 230 : 1286-1290. 1936.
4. CROSSLEY, M. L., NORTHEY, E. H., and HULTQUIST, M. E. J. Am. Chem. Soc. 60 (9) : 2217-2222. 1938.
5. GREEY, P. H., MACLAREN, D. B., and LUCAS, C. C. Can. Med. Assoc. J. 40 (4) : 319-324. 1939.
6. KOLLOFF, H. G. J. Am. Chem. Soc. 60 (4) : 950-951. 1938.
7. LUCAS, C. C. Can. Med. Assoc. J. 39 (2) : 111-114. 1938.
8. LUCAS, C. C. and MITCHELL, D. R. Can. Med. Assoc. J. 40 (1) : 27-34. 1939.
9. MITCHELL, D. R., GREEY, P. H., and LUCAS, C. C. Can. Med. Assoc. J. 40 (4) : 336-342. 1939.
10. STEWART, J. J. Chem. Soc. 121 : 2555-2561. 1922.
11. WEBSTER, G. L. and POWERS, L. D. J. Am. Chem. Soc. 60 (7) : 1553-1555. 1938.

APPENDIX

THE DETERMINATION OF CHEMOTHERAPEUTIC ACTIVITY

By PHILIP H. GREEY

The importance of the many variable factors involved in biological experiments is illustrated by the difficulties encountered in testing new compounds for chemotherapeutic activity. For example, in the *in vitro* bacteriostatic tests the composition and temperature of the culture media, size of inoculum, and time of making the observation are important; the variable susceptibility of hosts, virulence of bacterial strains used, size of infecting dose of bacteria, time interval between infection and first treatment, size and frequency of doses given, duration of medication, and other factors affect the *in vivo* results. Without some mention of these points in a report, it is difficult to compare the assessments of activity performed in different laboratories.

Numerous preliminary experiments were necessary to evolve a technique suitable for this study. For this purpose, compounds of known chemotherapeutic activity, such as sulphanilamide and sulfapyridine, were used. The experimental conditions that most clearly demonstrated the bacteriostatic activity of these compounds against various species of bacteria were determined.

I. In Vitro Studies

Stock cultures of a number of recently isolated strains of seven bacterial species were maintained on appropriate solid media. Each compound was tested against several strains of the various species, and each experiment included a known chemotherapeutic agent, usually sulfapyridine, for comparison and also to serve as a control that the conditions of the experiment were such as to demonstrate bacteriostasis.

The *in vitro* studies were performed by adding weighed amounts of dry-sterilized compound to a known volume of sterile Hartley's broth under aseptic conditions, to give a 100 mg. % solution from which the following dilutions were prepared: 50, 25, 10, 5, 1, 0.1 mg. %. These were dispensed in 5 cc. amounts in sterile test tubes. After 24 hr. incubation any contaminated tubes were rejected and the remainder were inoculated with the test organism. The drug-broth cultures and appropriate controls were incubated at 37° C. and readings made 24 and 48 hr. after inoculation. Bacteriostatic activity was gauged by comparing the opacity produced by the growth in the control and drug-broth tubes. The lowest concentration of drug that showed a marked inhibition of growth when compared with the control was taken as the index of bacteriostatic activity.

The following plan of testing was ultimately adopted:

Strep. haemolyticus—One loopful of a 1 : 1000 dilution of a 24 hr. broth-culture to 5 cc. of drug-broth medium containing 0.20 cc. of sterile horse or ox serum.

Strep. viridans—One loopful of 1 : 1000 dilution of a 24 hr. broth-culture to 5 cc. of plain drug-broth medium.

Pneumococcus—One loopful undiluted 24 hr. broth-culture to 5 cc. of drug-broth medium containing 0.20 cc. of sterile horse or ox serum.

Staph. aureus, *B. coli*, *B. typhosus*, *B. proteus*—One loopful of 1 : 1,000,000 dilution of a 24 hr. broth-culture to 5 cc. of plain drug-broth medium. In the case of *Staph. aureus*, if marked activity was noted in plain broth, a repeat experiment was carried out using the drug-broth with added serum as described above.

II. In Vivo Studies

In vivo experiments were conducted solely with white mice except for the *M. tuberculosis* infections, which were studied in guinea pigs. In preliminary experiments the acute toxicity of the compounds was determined by giving to pairs of animals the following doses of the drugs, dissolved or suspended in 5% gum acacia: 5, 25, 100, and 200 mg. If any of these animals died, the maximum tolerated dose was determined more accurately by repeating the procedure at smaller dosage intervals with larger groups of animals. The figures given in Table III, under the heading "acute toxicity" are, first, the largest test dose causing no deaths, and, second, the smallest test dose that caused all the animals to die. No attempt was made to determine the resulting concentrations of drug in the blood, so no data are available as to how much absorption of the compounds actually occurred. The size of the individual doses used in the *in vivo* tests was usually about one-twelfth the maximum tolerated dose, or if this proved to be more than 10 mg., only 10 mg. was given. (In some cases where no *in vitro* activity was observed, the *in vivo* tests were not done.) The drugs suspended in gum acacia were then administered, by stomach tube, according to the following plan:

First day—at time of infection, 3, 6, and 10 hr. later.

Second, third, and fourth days—at 9 a.m., 1, 5, and 11 p.m.

Fifth, sixth, and seventh days—at 9 a.m., 1, and 5 p.m.

TABLE III

ANTIBACTERIAL ACTIVITY OF THE COMPOUNDS PREPARED

Compound No.	Acute toxicity, mg. per mouse	*In vitro**				*In vivo***			
		Strep.	Pneu.	Staph.	B. Coli	Strep.	Pneu.	Staph.	M. Tb.
1	> 50 <100	+++	+++	++	++	++	0	0	0
2	>400	++	+++		+		0		0
3	>200	0	0	0	0		0	+	
4	>200					++	+		
5	>200					++	0	0	
6	>200	0	0	0	0		0		
7	>100 <150	0			0		0		
8	>200	++	+	0	+	++	0	++	0
9	>200	+	+	0	+		+	0	
10	>200	+	+	+	0	±	0		
11	>200						0		
12	>200					+	0	±	
13	>150 <200						0		
14	>200					+	0	0	
15	>200	+	+	0	0		+		±
16	>400	+	+++		0		0	0	0
17	>400	++	+++		0		+	0	0
18	>200	+	+	0	0		0		0
19	>400	0	++		0		0	0	0
20	>200	0	0	0	0		0		
21	>400	0	0		0		+		0
22	>200	++	+	+	0	±	0		
23	>150 <200	++	+++	++	0	+	+	±	
24	>200						0	+	
25	>200						0		
26	>200						0		
27	>200					0	0		
28	>200	0	0	0	0		+		
29	>400	0	+		0		0		0
30	>200	0	0	0	0		0		
31	>200	0	+	0	+		0	±	
32	>200	0	0	0	0	±	0		
33	>200	0	0	0	0		0		
34	>200	+	+	0	0		0		0
35	>200		0	0	+		0	0	
36	>200	0	0	0	0		0		
37	>200	0	0	0	0	+	0		
38	>200					+	0		
S†		++++	+++	±	++	++++	+	±	+
SP		++++	++++	±	+++	++++	++++	++	+
ST		++++	++++	+++	++++	++++	++++	+++	
SD		++++				++++	++++	+++	

* *The relative activity is expressed by symbols with the following significance:*
++++ *bacteriostatic at concentrations less than 10 mg. per 100 cc.*
+++ *bacteriostatic at concentrations less than 25 mg. per 100 cc.*
++ *bacteriostatic below 50 mg. per 100 cc.*
+ *bacteriostatic below 100 mg. per 100 cc.*
0 *not bacteriostatic at 100 mg. per 100 cc.*

** ++++ *at least 75% survivors.*
+++ *at least 40% survivors.*
++ *definite prolongation of survival time.*
+ *slight prolongation of survival time.*

† *S* = *sulphanilamide.*
SP = *sulfapyridine.*
ST = *sulfathiazole.*
SD = *sulfadiazine.*

Eighth and ninth days—at 9 a.m. and 5 p.m.

Tenth day—at 9 a.m.

A small group of normal (uninfected) animals received the same doses of drug as the treated animals. These served as "chronic toxicity" controls.

Experimental infections were produced in groups of 10 mice as follows:

Strep. haemolyticus

The mouse-virulent strain C203 was used. The organism was grown for 18 hr. in blood-broth directly from the heart's blood of a passage-mouse. This culture was diluted to 1 : 500,000 and 0.5 cc. injected intraperitoneally.

Pneumococcus

A Neufeld strain of *Pneumococcus* Type I was used. An 18 hr. broth-culture made from the heart's blood of a passage-mouse was diluted in broth to 1 : 5,000,000 and 0.5 cc. injected intraperitoneally.

Staph. aureus

The pathogenicity for mice of a number of strains isolated from patients in the wards of the Toronto General Hospital was determined and the strain (Kutt) possessing the greatest virulence selected for use. A culture, isolated the day before, from the heart's blood of a passage-mouse was used to plant blood-agar slopes. The growth on the slope after 20 hr. incubation was washed off with 6 cc. of Hartley's broth. Infection was initiated by the intravenous route, 0.2 cc. of the dense staphylococcal suspension being given to each mouse.

Each lot of compounds tested *in vivo* included a known chemotherapeutic agent—sulphanilamide, sulfapyridine, or sulfathiazole—so that the relative therapeutic merits of the compounds could be compared under identical conditions. Treated animals were kept under observation for 30 days. Mice dying despite treatment were autopsied and suitable cultures made to determine the cause of death.

Mycobacterium tuberculosis

Multicoloured guinea pigs weighing about 350 gm. were infected subcutaneously in the right thigh with 0.2 cc. of a suspension of human tubercle bacilli. This suspension was so prepared that each oil-immersion field contained approximately five acid-fast bacilli. Drug therapy was begun the day before infection was initiated and was continued daily thereafter until death of the animal. The drugs were given by mouth; with the aid of a nasal speculum an appropriate number of small tablets (25 mg.) were dropped at the back of the throat. Four doses (250 mg. per kg.) were given each day, at 9 a.m., 1, 5, and 11 p.m.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. FEBRUARY, 1942 NUMBER 2

CONTRIBUTION À L'ÉTUDE DES SEMICARBAZIDES δ-SUBSTITUÉES[1]

II. SEMICARBAZONES DE QUELQUES ALDÉHYDES ET CÉTONES

PAR ROGER BARRÉ[2] ET LUCIEN PICHÉ[3]

Sommaire

La transformation semicarbazide$\rightleftarrows$semicarbazone est une réaction réversible, qui donne lieu à un équilibre; théoriquement, du point de vue purement énergétique, la condensation d'une aldéhyde ou d'une cétone avec la semicarbazide simple ou substituée ne fournit jamais un rendement théorique de semicarbazone. Il est cependant démontré qu'on peut obtenir une réaction complète si on ajuste à leur optimum les conditions qui favorisent la condensation et surtout si on élimine la semicarbazone au fur et à mesure de sa formation.

Nous avons étudié plusieurs semicarbazides δ-substituées au point de vue de la solubilité relative de leurs semicarbazones; de tous ces dérivés, la *p*-nitrophényl-4-semicarbazide est celui qui présente les caractères les plus favorables à la précipitation des aldéhydes et des cétones. Son aptitude réactionnelle, sa stabilité, sa facilité relative de préparation et la faible solubilité de ses semicarbazones en font un réactif excellent des substances carbonylées; elle fournit un précipité quantitatif avec l'acétone, la benzaldéhyde, l'acétophénone, la *m*-nitrobenzaldéhyde, la vanilline, etc. Aussi la recommendons-nous comme réactif d'identification et de dosage des aldéhydes et des cétones.

Introduction

Pour l'identification et l'isolement des aldéhydes et des cétones, la semicarbazide compte au nombre des meilleurs réactifs; elle possède ce que Michael (8) a défini comme un "potentiel d'affinité élevé". Avec les sucres, elle conduit à des semicarbazones peu solubles et bien cristallisées, sans passer par l'intermédiaire de réactions antagonistes d'oxydo-réduction, comme cela se produit lors de la formation des osazones (7).

A cause du caractère essentiellement réversible de la réaction de condensation de la semicarbazide avec les aldéhydes et les cétones, la formation des semicarbazones est évidemment limitée, à chaque température et pour chaque composition du milieu réactionnel, par la réaction inverse d'hydrolyse. Depuis quelque temps, on a cherché à déterminer quels sont les facteurs qui fixent l'équilibre inévitablement atteint par la réaction en milieu homogène (3, 4); on s'est aussi appliqué à étudier les variations de vitesse de la condensation ou de la réaction inverse d'hydrolyse, en fonction de la nature du milieu (1, 5, 10).

---

[1] *Manuscrit original reçu le 9 octobre 1941, et sous forme revisée le 12 janvier 1942.*
Contribution de l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, Qué.

[2] *Professeur titulaire de chimie organique à la Faculté des Sciences.*

[3] *Chargé de cours en chimie générale, Faculté des Sciences.*

En système homogène, lorsque la solution est suffisamment diluée pour empêcher la précipitation de la semicarbazone, la réaction ne peut pas théoriquement conduire à un rendement quantitatif de semicarbazone; à chaque instant de la condensation, la vitesse est proportionnelle au produit des concentrations des deux substances à combiner et elle tend plus ou moins rapidement vers l'équilibre; il faut toutefois prévoir, en se basant sur les propriétés générales des équilibres chimiques, que la réaction sera complète si, ajustant à leur optimum les conditions qui accélèrent la condensation, on favorise en même temps l'élimination d'au moins un des produits de la réaction.

Cet objectif est en partie atteint si l'on opère en solution concentrée; le milieu se sature rapidement de semicarbazone relativement peu soluble; et l'élimine sous forme de précipité. On y arrive toutefois d'une façon plus efficace en utilisant la semicarbazide sous forme de combinaison à un radical organique de poids moléculaire élevé, rendant moins solubles les semicarbazones qui résultent de sa réaction avec les aldéhydes et les cétones. C'est en vue de ce résultat, déjà connu pour les hydrazones et d'ailleurs observé pour les semicarbazones elles-mêmes (6, 9, 11), que nous avons préparé plusieurs dérivés de la phényl-4-semicarbazide (2).

Partie expérimentale et résultats

L'influence relative des radicaux aromatiques sur la solubilité dans l'eau des semicarbazones substituées est exposée dans le Tableau I des solubilités respectives des semicarbazones fournies, par exemple, avec l'acétone et le glucose. Les semicarbazones du glucose figurent dans ce tableau parce que le principal objectif de notre travail était de déterminer quel dérivé de la semicarbazide se prête le mieux à des essais de précipitation quantitative de ce sucre.

L'examen de ces données révèle que la solubilité des semicarbazones ne dépend pas, rigoureusement de l'ordre de grandeur de leur poids moléculaire,

TABLEAU I

SOLUBILITÉ DANS L'EAU DES SEMICARBAZONES δ-SUBSTITUÉES DE L'ACÉTONE ET DU GLUCOSE

Semicarbazides	P.M.	Acétone-semicarbazone		Glucose-semicarbazone	
		P.M.	Solubilité, % (20° C.)	P.M.	Solubilité, % (20° C.)
Semicarbazide simple	75.1	115.1	6.22	237.2	2.25
Phényl-4-semicarbazide	151.1	191.2	0.09	313.2	7.57
p-Bromophényl-4-semicarbazide	230.0	270.1	0.02	392.1	0.64
p-Nitrophényl-4-semicarbazide	196.1	236.1	0.006	358.2	0.19
o, *p*-Dinitrophényl-4-semicarbazide	241.1	281.1	0.001	403.2	—
Benzyl-4-semicarbazide	165.1	205.1	0.20	327.2	11.50
Diphényl-4,4-semicarbazide	227.1	267.2	—	389.3	0.40
p-Xényl-4-semicarbazide	227.1	267.2	0.0002	389.3	0.05
p-Nitroxényl-4-semicarbazide	272.1	312.2	0.0001	434.2	—
Xanthyl-4-semicarbazide	257.1	297.2	0.002	419.3	0.03

mais bien plus de la nature du radical substituant qu'elles contiennent. Les dérivés les moins solubles sont fournis par les radicaux xényle (*p*-biphényle) et xanthyle, mais leurs semicarbazones cristallisent avec difficulté et se présentent sous forme de gelées qui retiennent toujours avec énergie une certaine quantité d'eau. Il est cependant possible de les isoler, pour fins d'identification et d'analyse, en les préparant dans l'alcool absolu et en distillant presque à sec après la condensation.

La présence du groupement nitré est nettement favorable à l'insolubilisation des semicarbazones et son influence se compare avantageusement à celle du groupement bromé ou à celle d'un second noyau benzénique. La *p*–nitrophényl–4–semicarbazide, en particulier, est caractérisée par une stabilité, par une rapidité et une uniformité d'action telles que de toutes les semicarbazides que nous ayons eu l'occasion de combiner avec les aldéhydes et les cétones, elle est celle qui se prête le mieux à leur identification par précipitation quantitative. Voici les points de fusion des semicarbazones que ce réactif nous a fournis avec les aldéhydes et les cétones suivantes (points de fusion instantanée; méthode Maquenne, indices non corrigés):—

p-Nitrophényl-4-semicarbazones	P.F., ° C.
Acétone..............................	264
Benzaldéhyde..........................	235 236
m-Nitrobenzaldéhyde	276
Vanilline..............................	261
Acide glyoxylique........................	249
Acide pyruvique.........................	261
Glucose...............................	192-193

Ces semicarbazones peuvent servir au dosage des substances carbonylées correspondantes; la précipitation est rapide et totale et elle est pratiquement indépendante de la nature du milieu où elle se produit.

Ces caractères, comparés aux propriétés équivalentes des nombreux dérivés hydraziniques ou semicarbazidiques qui sont utilisés comme réactifs de dosage des aldéhydes ou des cétones, nous laissent la conviction que la *p*-nitrophényl-4-semicarbazide est, pour cet usage, le réactif le plus efficace et le mieux adapté.

TABLEAU II

POINTS DE FUSION (° C.) DES DÉRIVÉS DE QUELQUES SEMICARBAZIDES δ-SUBSTITUÉES

Semicarbazides	Base libre	Chlorhydrate	Acétone-semi-carbazone	Glucose-semi-carbazone
Phényl-4-semicarbazide	123	215	160-1	*161*
p-Bromophényl-4-semicarbazide	254	218–21	174	*168*
p-Nitrophényl-4-semicarbazide	*191*	*215*	*264*	*192–3*
o, *p*-Dinitrophényl-4-semicarbazide	*178*	—	*248*	—
Benzyl-4-semicarbazide	111	224	113	*115*
p-Nitrobenzyl-4-semicarbazide	*164*	*195–7*	*162*	—
Diphényl-4,4-semicarbazide	154	218–20	119	164-6
p-Xényl-4-semicarbazide	258	*308*	*228*	*194*
p-Nitroxényl-4-semicarbazide	*178*	*219*	*261*	*172*
Xanthyl-4-semicarbazide	174	—	265	*183*

Pour servir d'indices d'identification, nous donnons dans le Tableau II, les points de fusion des semicarbazones de l'acétone et du glucose que nous avons obtenus avec quelques dérivés de la semicarbazide; les indices en italiques correspondent à des déterminations originales.

Conclusions

En dépit du caractère essentiellement réversible de la réaction de condensation des dérivés semicarbazidiques avec les aldéhydes et les cétones, il est possible d'obtenir un rendement quantitatif de semicarbazones, grâce à la faible solubilité de quelques-unes de celles-ci. Les caractères tout à fait particuliers de la *p*-nitrophényl-4-semicarbazide, sa stabilité, son uniformité d'action et l'insolubilité de ses semicarbazones nous la font recommander comme réactif d'identification et de dosage des substances carbonylées.

Bibliographie

1. ANZIANI, M. P. Bull. Soc. chim. Mém. (Sér. 5) 6 : 954-957. 1939.
2. BARRÉ, R. et PICHÉ, L. Can. J. Research, B, 19 : 158-171. 1941.
3. BARTLETT, P. D. J. Am. Chem. Soc. 54 : 2853-2858. 1932.
4. BARTLETT, P. D. J. Am. Chem. Soc. 55 : 741-749. 1933.
5. CONANT, J. B. et BARTLETT, P. D. J. Am. Chem. Soc. 54 : 2881-2899. 1932.
6. LEI, H.-H., SAH, P. P. T., et SHIH, C. J. Chinese Chem. Soc. 3 : 246-250. 1935.
7. MAQUENNE, L. et GOODWIN, W. Bull. soc. chim. Mém. (Sér. 3) 31 : 1075-1078. 1904.
8. MICHAEL, A. J. Am. Chem. Soc. 41 : 393-424. 1919.
9. SAH, P. P. T., WANG, S.-M., et KAO, C.-H. J. Chinese Chem. Soc. 4 : 187-192. 1936.
10. WESTHEIMER, F. H. J. Am. Chem. Soc. 56 : 1962-1965. 1934.
11. WHEELER, A. S. et BOST, R. W. J. Am. Chem. Soc. 46 : 2813-2816. 1924.

THE IDENTIFICATION OF BIOS V AS VITAMIN B_1 AND OF A CONSTITUENT OF BIOS VII SOLUTION AS VITAMIN B_6; THEIR EFFECT UPON THE REPRODUCTION OF *SACCHAROMYCES HANSENIASPORA VALBYENSIS*, YEAST 2335, AND *SACCHAROMYCES GALACTOSUS*[1]

By Cosmo Marchant[2]

Abstract

Experiments described in this paper show that both *Saccharomyces hanseniaspora valbyensis* and Yeast 2335 require the presence of crude Bios IIA, purified Bios IIB, vitamin B_6 (in place of Bios VII solution), and vitamin B_1 (in place of Bios V solution) in addition to *meso*-inositol in the culture medium to ensure a good crop; that *Saccharomyces galactosus* requires crude Bios IIA, purified Bios IIB, Bios VII solution (not vitamin B_6), and vitamin B_1 (in place of Bios V solution). They further show that the intermediates used in the synthesis of vitamin B_1 when added to a medium containing no vitamin B_1 increase the crop of Yeast 2335 and of *S. galactosus*, but not of *S. hanseniaspora valbyensis*.

Introduction

The constituents of Bios which give good crops of *Saccharomyces cerevisiae* (1, 6, 10) are not sufficient to ensure good crops of certain other species of yeast. Miss Farrell (3), for instance, found that *Saccharomyces hanseniaspora valbyensis* needed not only *meso*-inositol, crude Bios IIA,[*] and crude Bios IIB,[*] but also some other constituent of wort, tomato juice, or yeast water. To this unknown she gave the name Bios V. Miss Elder (2) showed that, in addition to *meso*-inositol, purified Bios IIA,[*] purified Bios IIB[*] and Bios V, *S. hanseniaspora valbyensis* needs two others (not required by *S. cerevisiae*); one of these (Bios VII) is contained in the crude Bios IIB solution and the other (Bios VIII) in the crude Bios IIA solution. Maconachie (9) found that Yeast 2335 of the American Type Culture Collection required *meso*-inositol and Bios II (crude Bios IIA and crude Bios IIB). Miss Farrell and Miss Elder found that in media made up with (*a*) "Bios V Reagent",[**] (*b*) inositol, crude Bios IIA, and crude Bios IIB, and (*c*) tomato juice, *S. cerevisiae* gave crops of the same size, but *Saccharomyces galactosus* and

---

[1] *Manuscript received in original form August 25, 1941, and as revised, January 8, 1942.*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. From a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Toronto.

[2] *Assistant, Department of Chemistry, University of Toronto. At present, Lecturer, Department of Chemistry, Queen's University, Kingston, Ont.*

[*] *The term purified Bios IIA signifies that the crude Bios IIA solution has been freed of traces of Bios VIII as well as other impurities, while the term crude Bios IIA indicates that the solution contains both Bios VIII and purified Bios IIA. Similarly, crude Bios IIB solution contains both purified Bios IIB and Bios VII, while purified Bios IIB solution contains no Bios VII.*

[**] *"Bios Reagent" is obtained by adding tannin and basic lead acetate to tomato juice, filtering off the precipitate, heating the filtrate with excess calcium hydroxide at 100° C. for 40 min. to destroy Bios V, filtering, and removing excess lime by passing carbon dioxide into the hot solution. It thus contains all the constituents of Bios except Bios V.*

Yeast 2335 gave much smaller crops in (*a*) and (*b*) than in (*c*). Miss Elder also found that the addition of Bios V solution (in an amount that greatly increases the crop of *S. hanseniaspora valbyensis*) to media containing "Bios V Reagent" did not increase the crops of *S. galactosus* and Yeast 2335. She therefore drew the conclusion (later shown to be unjustified) that these two yeasts required at least one other unknown constituent which may or may not be the same for each yeast.

This paper describes the results of a study of Bios V, Bios VII, and Bios VIII and their effect upon the reproduction of *S. hanseniaspora valbyensis*, Yeast 2335, and *S. galactosus*.

Experimental

THE YEASTS

Saccharomyces hanseniaspora valbyensis (A.T.C.C. 2108)

This culture was obtained from the A.T.C.C. in 1930. During the course of these experiments a strain (*N*) of this yeast was isolated which, with a fixed amount of Bios, gave two-thirds the crop given by a strain (*II*) obtained from the Centralbureau voor Schimmelcultures in Delft in 1938. This Strain *II* was derived from the original A.T.C.C. culture, since in 1936 a culture of *S. hanseniaspora valbyensis* had been sent to Delft from Toronto. The only other way in which these strains differed was in the rates of reproduction: For the first 12 hr. the rates were about the same, but that of Strain *N* fell off after this time; Strain *II* attained its maximum crop between 24 and 28 hr., Strain *N* between 28 and 32 hr., and the maximum crop of *II* was higher than that of *N*. No difference was observed in cell size or the appearance of colonies and, so far, no difference in the constituents of Bios required by each strain has been observed.

Yeast 2335

A culture of this yeast was purchased from the A.T.C.C. in May 1936. Miss Elder (2) found that when this yeast was plated out, two types of colonies developed in the ratio of about one smooth colony with radial furrows to eight fuzzy colonies; yeast from either type of colony on subsequent plating out remained true to type. For the experiments described below, Miss Elder's race F (Fuzzy) was used.

Saccharomyces galactosus

This culture was kindly supplied in 1932 by Dr. A. M. Wynne, of the Department of Biochemistry, University of Toronto, who had obtained it from the Labatorium voor Microbiologie der Technische Hoogeschool at Delft.

PROCEDURE

The yeasts for seeding were cultivated by rocking at 25° C. in rocker tubes containing 10 cc. of tomato juice culture medium and transferring a loopful every 24 hr. to a fresh 10 cc. of medium (3, 9).

The method of Bios assay was the same as that described by Miss Elder (2).

EXPERIMENTS WITH BIOS V

Identification of Bios V as Vitamin B_1 (7)

On February 8, 1937, Dr. C. N. Frey of the Fleischmann Laboratories notified us that vitamin B_1 greatly accelerated the rate of fermentation of yeast (11). This substance (Merck's Betabion—vitamin B_1 hydrochloride) was at once tried, to ascertain whether it would replace any of the unknown constituents of the culture medium for *S. hanseniaspora valbyensis.*

The solutions used in all the experiments were prepared as follows. The inositol solutions were made from Eastman's Ash-free *meso*-inositol; the Bios V (acetone-purified) and "Bios V Reagent" were prepared by Miss Elder (2); the tomato juice was first freed of pulp, then neutralized (litmus) with sodium hydroxide and diluted to the required strength; the vitamin B_1 solutions were made from Merck's Betabion (thiamine hydrochloride) by dissolving in water, making slightly acid to litmus with acetic acid, and diluting to the desired strength; the crude Bios IIB, purified Bios IIB, and Bios VII solution were prepared as described on page 27; and the crude Bios IIA was prepared according to Miss Sanderson's recipe (5). The "concentrations" are cubic centimetres of tomato juice (t.j.) from which the solutions were formed, except where otherwise stated or where a particular chemical has been used. To every assay medium one constituent of Bios was added in a small amount so that it would be used up first and thus limit the size of the crop.

In Table I the crop-limiting constituent is either Bios VII solution or the Bios VII in the crude Bios IIB solution, when the latter is substituted for the purified Bios IIB and the Bios VII. It is obvious that for the purpose of this experiment it does not matter which constituent is present in the least (physiological) amount. The results (Table I) show that when vitamin B_1 replaced Bios V solution the crop was much larger than when the medium contained neither Bios V nor vitamin B_1 and was as large as that obtained when the medium contained Bios V; that when it was substituted for any of the other constituents, the crops were no larger than those obtained when any of them was omitted.

Subsequent experiments showed that vitamin B_1 can replace Miss Elder's "unknown constituent" for Yeast 2335 and *S. galactosus.*

Miss Elder (2) found that the addition of Bios V to media containing tomato juice did not increase the crop of *S. hanseniaspora valbyensis,* while the addition of "Bios V Reagent" did. In this respect also, vitamin B_1 is the same as Bios V. It follows that the amount of vitamin B_1 in the tomato juice is measured by the crop of *S. hanseniaspora valbyensis* only if the assay medium is made up with excess of "Bios V Reagent". On the other hand, with Yeast 2335 and *S. galactosus,* when a large quantity of vitamin B_1 (or Bios V) was added to media containing tomato juice the crops were greatly increased. As the addition of "Bios V Reagent", or inositol, crude Bios IIA, and crude Bios IIB, to a medium containing tomato juice did not increase the crop of either yeast, the constituent in the least (physiological) amount for these two yeasts is vitamin B_1. With this in mind, measurements were made to determine the concentration of vitamin B_1 in tomato juice. The results obtained with *S. hanseniaspora valbyensis* are given in Table II. The measurements with Yeast 2335 and *S. galactosus* were made with the concentrations of the constituents outlined below, and also with twice the concentrations of dextrose, salts, and "Bios V Reagent" shown in Table II.

TABLE I

THE EFFECT ON THE GROWTH OF *S. hanseniaspora valbyensis** OF REPLACING BIOS V, VII, AND VIII BY VITAMIN B_1

Each cubic centimetre of assay medium contained 50 mg. of dextrose, 2.1 mg. of potassium dihydrogen phosphate, 4.2 mg. of ammonium nitrate, 1.0 mg. of magnesium sulphate heptahydrate, 0.35 mg. of calcium chloride hexahydrate, and 0.02 mg. of inositol, together with the ingredients§ given below.

Crude Bios IIA from cc. t.j.	Crude Bios IIB from cc. t.j.	Purified Bios IIB from cc. t.j.	Bios VII from cc. t.j.	Bios V from cc. t.j.	Vitamin B_1 γ	Count**
0.1	0.033	0	0	0	0	30
0.1	0.033	0	0	0.0225	0	250
0.1	0.033	0	0	0	0.33	246
0	0.033	0	0	0.0225	0	187
0	0.033	0	0	0.0225	0.33	180
0.1	0	0.05	0.05	0.0225	0	260
0.1	0	0.05	0	0.0225	0	30
0.1	0	0.05	0	0.0225	0.33	40
0.1	0	0	0.05	0.0225	0	20
0.1	0	0	0.05	0.0225	0.33	30

* *The measurements recorded in Tables I, II, and IV were carried out before the culture of S. hanseniaspora valbyensis had been shown to be a mixture of at least two strains. This does not invalidate the results, however, since all the measurements in any one table were made at the same time with the same yeast suspension.*

§ *These solutions contain none, or only traces, of the other constituents of Bios, except; (a) the crude Bios IIB, which contains purified Bios IIB and Bios VII; (b) crude Bios IIA, which contains purified Bios IIA and Bios VIII; and (c) "Bios V Reagent", which contains all constituents except Bios V.*

** *A count (C) of 1.0 = 250,000 cells per cc.*

It was soon seen that the amounts of vitamin B_1, tomato juice, and Bios V solution required to secure a given crop of Yeast 2335 are proportional to those required by *S. hanseniaspora valbyensis*, but from 67 to 87 times greater, and, as with *S. hanseniaspora valbyensis*, doubling the amounts of either Bios V solution or vitamin B_1 doubles the crop of Yeast 2335. To give a crop of about C = 252 the quantity of vitamin B_1 required by *S. galactosus* is about 31 times that required by *S. hanseniaspora valbyensis;* in contrast to what occurs with the other yeasts, doubling the amount multiplies the crop by 1.7. According to the experiments with *S. hanseniaspora valbyensis*, 1 cc. of tomato juice contains 0.57 γ of vitamin B_1; according to those with Yeast 2335, 0.62 γ; and those with *S. galactosus*, 0.54γ. The tomato juice

TABLE II

DETERMINATION OF THE CONCENTRATION OF VITAMIN B_1 IN TOMATO JUICE WITH *S. hanseniaspora valbyensis**

Each cubic centimetre of assay medium contained dextrose, salts, and "Bios V Reagent" from 0.09 cc. of tomato juice together with the ingredients given below

Tomato juice, cc.	Vitamin B_1, γ	Bios V from cc. t.j.	Vitamin B_1§, γ	Count
0	0	0	0	20
0.0015	0	0	0	320
0.0020	0	0	0	460
0	0.00062	0	0	238
0	0.00087	0	0	306**
0	0.00093	0	0	360
0	0.00124	0	0	527
0	0	0.0103	0	221
0	0	0.0145	0	320
0	0	0.0154	0	380
0	0	0.0206	0	440
0	0	0	0.00124	20

* *See footnote Table I.*

§ *Ten cc. of a solution containing 0.0062γ of vitamin B_1 per cc. was heated for 30 min. at 100° C. with 0.5 gm. of calcium hydroxide, filtered, and the excess lime removed by passing carbon dioxide into the hot solution. Two cc. of this solution was added to the assay medium.*

** *In identical assay media, Strain N gives a count of 240 and Strain H one of 360.*

used in the experiments was from a small tin of Libby's (Libby McNeill and Libby of Canada Ltd.) tomato juice. A later shipment of No. 10 tins of Libby's contained about 0.3γ vitamin B_1 per cc.; Silver Ribbon Brand (Baxter Canning Co.) tomato juice contained about 0.4γ per cc.

Since, to give about the same crop, Yeast 2335 and *S. galactosus* require much more vitamin B_1 than *S. hanseniaspora valbyensis*, it is easy to understand why Miss Elder failed to get any increase in the crops of these two yeasts, for she used the same amounts of Bios V as in her experiments with *S. hanseniaspora valbyensis*.

Both vitamin B_1 and Bios V occur in fruit juices, wort, and yeast water (3); the behaviour of the former with reagents, particularly the destruction of its activity on heating with lime water (Table II), is the same as that of Bios V; so there need be no hesitation in concluding that the active constituent of Bios V solution and that required by Yeast 2335 and *S. galactosus* is vitamin B_1.

THE EFFECT OF REPLACING VITAMIN B_1 BY "AMINOPYRIMIDINE" AND "THIAZOLE" (8)

In 1938, Dr. C. N. Frey *et al.* (12) reported that, with certain races of yeast, vitamin B_1 could be replaced by the intermediates used in its synthesis, viz.: 2-methyl-5-ethoxymethyl-6-aminopyrimidine and 4-methyl-5-β-hydroxyethylthiazole. A few milligrams of the "aminopyrimidine" was very kindly sent to us by Dr. Frey; for the "thiazole" we are indebted to Merck and Company Inc.

It was found that the "aminopyrimidine" and the "thiazole" when added singly or together to the assay medium produce little or no increase in the crop of either strain of *S. hanseniaspora valbyensis*. In other words, with *S. hanseniaspora valbyensis* vitamin B_1 cannot be replaced by its intermediates.

With Yeast 2335, addition of the "aminopyrimidine" alone has little effect on the crop; addition of 0.005γ of "thiazole" increases it, but it is not much further increased by adding 20 times that amount. Addition of "aminopyrimidine" to media containing "thiazole" increases the crop, but the addition of more and more of both does not increase it above C = 320 whether the assay medium contains "Bios V Reagent" from 0.2 cc. or from 0.3 cc. of tomato juice.

The crops obtained in media containing mixtures of the intermediates or "thiazole" alone are greater (at the lower concentrations) and smaller (at the higher concentrations) than those that would be obtained from the amount of vitamin B_1 that could be formed from them according to the equation:

$$\begin{array}{lclcl} C_8H_{13}N_3O & + & C_6H_{10}NSO & = & C_{12}H_{18}N_4SOCl_2 \\ 167.1\gamma & & 144.1\gamma & & 337.1\gamma \\ \text{"Aminopyrimidine"} & & \text{"Thiazole"} & & \text{Vitamin } B_1 \\ & & & & \text{hydrochloride} \end{array}$$

For, 0.012γ of vitamin B_1 (= 0.006γ of "aminopyrimidine" + 0.005γ of "thiazole", for which C = 110) would give a crop of C = 54, and 0.12γ of vitamin B_1 (= 0.06γ of "aminopyrimidine" + 0.05γ of "thiazole"; C = 320) would yield one of C = 540.

With *S. galactosus* (Table III), "thiazole" by itself has little or no effect on the crop (cf. Yeast 2335); 0.005γ of "aminopyrimidine" gives one of C = 178, while even 20 times that amount of "aminopyrimidine" gives a count only slightly higher.

TABLE III

THE EFFECT OF REPLACING VITAMIN B_1 WITH "AMINOPYRIMIDINE" AND "THIAZOLE"

Each cubic centimetre of assay medium contained dextrose and salts (twice the concentrations shown in Table I), inositol* and crude Bios IIA* from 0.2 cc. of tomato juice, and crude Bios IIB from 0.118 cc. of tomato juice, together with the ingredients given below

"Amino-pyrimidine" γ	"Thiazole" γ	Count	"Amino-pyrimidine" γ	"Thiazole" γ	Count
0	0	88	0	0.1	97
0.005	0	178	0.005	0.005	200
0.01	0	212	0.01	0.01	262
0.05	0	239	0.01	0.1	294
0.1	0	221	0.1	0.01	433
0	0.005	105	0.05	0.05	735
0	0.01	88	0.1	0.1	714
0	0.05	106			

* *For convenience, the charcoal filtrate (p. 27), which contains both meso-inositol and crude Bios IIA, was used in making up the assay media.*

Mixtures of the "intermediates" in amounts that are approximately equivalent to a given amount of vitamin B_1 give about the same crop as the vitamin B_1 when they replace it in the culture medium for *S. galactosus.* For example, 0.02γ of vitamin B_1, which is equivalent to 0.01γ of "aminopyrimidine" + 0.0084γ of "thiazole", gives a count of 252, while 0.01γ of "aminopyrimidine" + 0.01γ of "thiazole" gives a count of 262.

EXPERIMENTS WITH BIOS VII

The Preparation of Bios VII Solution

As the Bios IIB solution from sugar-refinery charcoal (7) contained no Bios VII,* that substance could not be used as a raw material. In order to obtain a sufficient quantity of Bios VII solution, 72 kg. of tomato juice (Silver Ribbon Brand, Baxter Canning Company) were worked up according to Miss Sanderson's recipe (5) in 14.4 kg. batches. And the crude Bios IIB was obtained by adsorption on charcoal after the method of Sparling (10). The 54 cc. of crude Bios IIB thus prepared contained 16% of the Bios VII present in the tomato juice from which it was obtained.

The Fractionation of Crude Bios IIB into Purified Bios IIB and Bios VII

To 1 cc. (0.93 gm. of non-volatile matter) of a neutral crude Bios IIB solution, 0.45 cc. of 10% sodium carbonate solution and 0.5 cc. of 25% mercuric acetate solution were added alternately four times. The volume was then brought to 34 cc. with 95% ethyl alcohol. After standing three hours, the precipitate (I) was filtered off. The filtrate was evaporated *in vacuo* to a volume of 1 cc. and the whole process repeated; but this time a total of 3.6 cc. of 10% sodium carbonate solution and 4.4 cc. of the mercury solution was used, then made up to 60 cc. with 95% alcohol. This precipitate (II) was filtered off after three hours. The mercury was removed as sulphide from all three fractions, viz.; the first and second precipitates and the final filtrate (the precipitates were suspended in dilute acetic acid solution for this operation). The resulting solutions were all brought to the same concentration, viz.; 1 cc. of solution from 0.33 cc. of tomato juice. The data regarding the crops of *S. hanseniaspora valbyensis* obtained with these solutions are given in Table IV.

The results show that the crops obtained in media containing either (*a*) the first precipitate, second precipitate, and final filtrate, or (*b*) the second precipitate and final filtrate, were almost as large as the crop obtained in a medium containing that amount of crude IIB from which the solutions had been obtained. In media containing any one by itself or any other combination of the solutions, the crop was small. Thus crude Bios IIB can be fractionated into two constituents (second precipitate and final filtrate), neither of which by itself gives any appreciable crop of *S. hanseniaspora valbyensis,*

---

* *Two relatively impure preparations of IIB from sugar-refinery charcoal were tried with S. hanseniaspora valbyensis. Neither replaced crude IIB, nor was either a poison; both could replace purified Bios IIB.*

TABLE IV

THE EFFECT OF THE FRACTIONS FROM CRUDE BIOS IIB ON THE REPRODUCTION OF *S. hanseniaspora valbyensis**

Each cubic centimetre of assay medium contained dextrose and salts, 0.02 mg. of inositol, crude Bios IIA from 0.01 cc. of tomato juice, and Bios V from 0.0225 cc. of tomato juice, together with the ingredients given below

Crude Bios IIB from cc. t.j.	Ppt. I from cc. t.j.	Ppt. II from cc. t.j.	Filtrate from cc. t.j.	Count
0	0	0	0	12
0.033	0	0	0	210
0	0.033	0.033	0.033	180
0	0.033	0.033	0	20
0	0	0.033	0.033	160
0	0.033	0	0.033	51
0	0.033	0	0	5
0	0	0.033	0	8
0	0	0	0.033	17

* *See footnote Table I.*

while both together give a large crop. The one that is not precipitated by mercury carbonate is Bios VII; the other is purified Bios IIB.

The remainder of the crude Bios IIB solution was treated in a similar manner with mercury carbonate. The final filtrate (after removing mercury as the sulphide) contained about 30% of the Bios VII present in the 54 cc. of crude IIB solution, i.e., about 5% of that in the 72 kg. of tomato juice. It was almost free of purified Bios IIB. The amount of non-volatile matter per unit of Bios VII* was 0.86 mg.; most of this was sodium acetate.

Removal of Sodium from the Bios VII Solution

The greater part of the sodium was removed by adding 31.2 cc. of 18.4 *N* sulphuric acid, evaporating *in vacuo* to remove the acetic acid, and extracting the dry residue with 680 cc. of 95% ethyl alcohol; this left most of the sodium sulphate behind. The alcoholic solution was evaporated *in vacuo* to dryness, and the residue was stirred with water; an appreciable amount remained undissolved. The aqueous solution was evaporated *in vacuo* to dryness, dissolved again in water, and a small amount of sulphate was removed as barium sulphate. After filtering, the solution contained 96% of the Bios VII present before the removal of sodium and only 17% of the non-volatile matter; quality, 0.15 mg./unit.

Further Purification with Alcohol

The solution of Bios VII so obtained was evaporated to dryness *in vacuo* and stirred with 600 cc. of 95% ethyl alcohol. A considerable amount of material was left undissolved. The alcoholic solution was evaporated to dryness; nearly all the residue dissolved in water. The aqueous solution was evaporated to dryness and the residue dissolved again in water. After these operations there remained 98% of the Bios VII, whereas the amount of non-volatile matter was reduced by 28%; quality, 0.11 mg./unit.

---

* *Defined as that amount which, when all the other constituents are present in excess in the assay medium, gives a crop of C = 300 to 350 with S. hanseniaspora valbyensis N.*

The Identification of a Constituent of Bios VII Solution as Vitamin B_6(8)

In August, 1938, shortly after a note (4) appeared reporting the isolation of pure crystals of the hydrochloride of vitamin B_6, Merck and Co. Inc. very kindly sent a milligram of this compound to us.

It was immediately found that both *S. hanseniaspora valbyensis N* and *H* gave a large crop in a medium containing inositol, crude IIA, vitamin B_1, and purified Bios IIB to which had been added vitamin B_6 (1.0γ per cc.) in place of Bios VII; but when vitamin B_6 was tried in place of Bios IIB the crop was small.

As in the case of vitamin B_1, experiments were carried out to determine the amounts of vitamin B_6 and Bios VII solution required to secure a given

TABLE V

DETERMINATION OF THE CONCENTRATION OF VITAMIN B_6 IN TOMATO JUICE WITH *S. hanseniaspora valbyensis*

Each cubic centimetre of assay medium contained dextrose, salts, inositol from 0.2 cc. of tomato juice, crude Bios IIA from 0.2 cc. of tomato juice, and 0.154 γ of vitamin B_1, together with the ingredients given below

Purified Bios IIB§, γ	Tomato juice, cc.	Bios VII*, cc. t.j.	Vitamin B_6, γ	Count	
				N	*H*
1.39	0	0	0	68	68
1.39	0.0013	0	0	—	180
1.39	0.0025	0	0	200	300
1.39	0.005	0	0	330	500
1.39	0.01	0	0	510	—
1.39	0	0.025	0	—	174
1.39	0	0.05	0	200	280
1.39	0	0.1	0	310	470
1.39	0	0.2	0	460	—
1.39	0	0	0.0005	—	170
1.39	0	0	0.001	190	238
1.39	0	0	0.00125	—	260
1.39	0	0	0.002	290	408
1.39	0	0	0.0025	340	—
1.39	0	0	0.004	430	—
0	0.0025	0	0	—	309
0	0.005	0	0	357	—
0	0	0.05	0	—	42
0	0	0.1	0	68	—
0	0	0	0.00125	—	25
0	0	0	0.0025	25	—

§ *This was prepared from sugar-refinery charcoal by extracting the charcoal with ethyl alcohol and ammonia, evaporating to dryness, taking up in water, and again evaporating to dryness. The residue was further purified by heating with methyl alcohol and hydrochloric acid and extracting with chloroform; this operation was repeated using ethyl alcohol. The concentration is expressed as the weight of non-volatile matter per cubic centimetre.*

* *This preparation contained 4.7% of the Bios VII present in the tomato juice from which it was prepared; therefore the preparation from 0.1 cc. of tomato juice should contain the Bios VII of 0.0047 cc. of tomato juice; this is so, for, in this table, 0.005 cc. of tomato juice was used.*

crop and to determine the concentration of vitamin B_6 in tomato juice. From the results of Table V it is seen that, with both *S. hanseniaspora valbyensis N* and *H*, vitamin B_6 can replace Bios VII solution; that, in contrast to what occurs with vitamin B_1 or Bios V, doubling the quantities of tomato juice, Bios VII solution, or vitamin B_6, multiplies the crop by about only 1.6; and that 1 cc. of tomato juice or Bios VII solution from 20 cc. of tomato juice can replace 0.4 to 0.5γ of vitamin B_6 whether the crop of *S. hanseniaspora valbyensis N* or *H* be measured.

While this manuscript was in preparation, a note (13) from Frey *et al.* appeared announcing that vitamin B_6 could replace vitamin B_1 in the culture medium for certain of his yeasts. Consequently, measurements were made to ascertain whether this would hold for *S. hanseniaspora valbyensis*. In contrast to Frey's findings with his yeasts, vitamin B_6 cannot replace vitamin B_1 in the culture medium for *S. hanseniaspora valbyensis II.*

TABLE VI

DATA SHOWING VITAMIN B_6 CANNOT REPLACE VITAMIN B_1 IN THE CULTURE MEDIUM FOR *S. hanseniaspora valbyensis*

Each cubic centimetre of assay medium contained dextrose, salts, 0.04 mg. of inositol, crude Bios IIA from 0.1 cc. of tomato juice, and crude Bios IIB from 0.033 cc. of tomato juice, together with the ingredients given below

Vitamin B_1	Vitamin B_6	Count
0	0	50
0.00087	0	350
0	0.00125	60

Measurements made with Yeast 2335 showed that small crops of this yeast were obtained in a medium containing inositol, crude Bios IIA, and vitamin B_1, but neither purified Bios IIB nor Bios VII solution; a somewhat larger crop when either purified Bios IIB or Bios VII solution was added; and a much larger crop when both were added together. Moreover, vitamin B_6 can replace Bios VII solution. Doubling the amounts of tomato juice, Bios VII, or vitamin B_6 multiplies the crop by about 1.4 (contrast vitamin B_1 or Bios V); to secure a crop of $C = 300$, about four times the quantity of Bios VII solution or vitamin B_6 required by *S. hanseniaspora valbyensis N* is necessary. The results also confirmed those of Table V, namely, that 1 cc. of tomato juice or Bios VII solution from 20 cc. of tomato juice contains 0.4 to 0.5γ of vitamin B_6.

Thus the active principle for *S. hanseniaspora valbyensis* and Yeast 2335 in the Bios VII solution is vitamin B_6.

On the other hand, small crops of *S. galactosus* were obtained in media containing (besides inositol, crude Bios IIA, and vitamin B_1) either Bios VII solution or purified Bios IIB and vitamin B_6, but when the medium contained inositol, crude Bios IIA, vitamin B_1, purified Bios IIB, and Bios VII solution the crop was large.

Therefore, *S. galactosus*, like the others, requires purified Bios IIB and Bios VII solution, but as the latter cannot be replaced by vitamin B_6, it must be assumed either that the Bios VII solution contains two active constituents, viz., vitamin B_6 and the constituent required by *S. galactosus*, or that there is some chemical other than vitamin B_6 that behaves with *S. hanseniaspora valbyensis* and Yeast 2335 just as vitamin B_6 does.

EXPERIMENTS WITH BIOS VIII

When it was discovered that, with *S. cerevisiae*, Bios IIA can be replaced by β-alanine alone or *l*-leucine plus β-alanine (6), the same replacements were tried with *S. hanseniaspora valbyensis*, Yeast 2335, and *S. galactosus.*

The results showed that β-alanine (about 200 times the amount used with *S. cerevisiae*) alone or β-alanine plus *l*-leucine cannot replace crude Bios IIA in the culture medium for *S. hanseniaspora valbyensis*, but they did not show whether β-alanine and *l*-leucine are constituents of Bios for this yeast in addition to the unknown constituent (Bios VIII) in the crude Bios IIA.

The similar measurements made with Yeast 2335 and *S. galactosus* showed that β-alanine plus *l*-leucine cannot take the place of crude Bios IIA with either yeast, but did not show whether β-alanine and *l*-leucine are necessary to ensure good crops of these yeasts.

Thus, the production of good crops of the three yeasts requires the presence, in the culture medium, of some unknown constituent (perhaps the same for all) called provisionally Bios VIII, which is present in the crude Bios IIA solution.

Acknowledgments

The writer wishes to acknowledge his indebtedness to the late Dr. W. Lash Miller, under whom this work was carried out, for his kindness and assistance.

This research was aided by a grant from Standard Brands of Canada Limited.

References

1. EASTCOTT, E. V. J. Phys. Chem. 32 : 1094-1111. 1928.
2. ELDER, M. L. Trans. Roy Soc. Can. (Ser. 3) 30 (Sec. 3) : 89-97. 1936.
3. FARRELL, L. N. Trans. Roy. Soc. Can. (Ser. 3) 29 (Sec. 3) : 167-173. 1935.
4. KERESZTESY, J. C. and STEVENS, J. R. J. Am. Chem. Soc. 60 : 1267-1268. 1938.
5. MILLER, W. L. Trans. Roy. Soc. Can. (Ser. 3) 28 (Sec. 3) : 185-187. 1934.
6. MILLER, W. L. Trans. Roy. Soc. Can. (Ser. 3) 30 (Sec. 3) : 99-103. 1936.
7. MILLER, W. L. Trans. Roy. Soc. Can. (Ser. 3) 31 (Sec. 3) : 159-162. 1937.
8. MILLER, W. L. Proc. Intern. Congr. Microbiol. 3rd Congr., pp. 498-499. 1939.
9. MILLER, W. L., EASTCOTT, E. V., and MACONACHIE, J. E. J. Am. Chem. Soc. 55 : 1502-1517. 1933.
10. MILLER, W. L., EASTCOTT, E. V., and SPARLING, E. M. Trans. Roy. Soc. Can. (Ser. 3) 26 (Sec. 3) : 165-169. 1932.
11. SCHULTZ, A., ATKIN, L., and FREY, C. N. J. Am. Chem. Soc. 59 : 948-949. 1937.
12. SCHULTZ, A., ATKIN, L., and FREY, C. N. J. Am. Chem. Soc. 60 : 490. 1938.
13. SCHULTZ, A., ATKIN, L., and FREY, C. N. J. Am. Chem. Soc. 61 : 1931. 1939.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. B. MARCH, 1942 NUMBER 3

CONTRIBUTION À L'ÉTUDE DES SEMICARBAZIDES δ-SUBSTITUÉES

III. ESSAI D'APPLICATION AU DOSAGE DU GLUCOSE[1]

PAR GEORGES H. BARIL[2], ROGER BARRÉ[3] ET LUCIEN PICHÉ[4]

Sommaire

Nous avons tenté d'adapter la *p*-nitrophényl-4-semicarbazide à une méthode de dosage gravimétrique du glucose.

La réaction de ce dérivé sur le dextrose fournit une molécule d'eau comme produit secondaire; afin de supprimer l'équilibre qui tend à limiter le rendement, cette eau est éliminée par évaporation au fur et à mesure de sa formation. On obtient ainsi en peu de temps un rendement quantitatif de glucose-*p*-nitrophényl-4-semicarbazone qu'on dose par précipitation à l'état de *m*-nitrobenzal-semicarbazone insoluble.

Cette méthode permet, sans défécation, de doser le glucose dans les milieux réducteurs; elle est applicable directement à des concentrations de glucose comprises entre 0.2 à 1.0% et peut atteindre une concentration limite de 0.1% par concentration préalable de la solution sucrée.

Introduction

Dans une communication précédente (2), nous avons signalé que les semicarbazides δ-substituées fournissent rapidement un rendement élevé, sinon théorique, de semicarbazones peu solubles lorsqu'on les fait réagir avec les aldéhydes ou les cétones. C'est en nous basant sur cette propriété que nous avons essayé de mettre au point une méthode de dosage gravimétrique du glucose. Nous nous sommes adressés à la *p*-nitrophényl-4-semicarbazide comme réactif parce qu'elle présente l'affinité et la stabilité nécessaires à cette fin.

Le procédé que nous proposons n'a pas la prétention d'être définitif; il se propose bien plus de démontrer la possibilité de baser un dosage du glucose sur une réaction spécifique, correspondant rigoureusement à une équation chimique et de la dégager ainsi des conditions aléatoires qui accompagnent la défécation des solutions et les méthodes à réduction d'un hydroxyde métallique en milieu alcalin.

---

[1] *Manuscrit original reçu le 9 octobre 1941, et sous forme revisée le 12 janvier 1942.*
Contribution de l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, Qué.

[2] *Directeur de l'Institut de Chimie.*

[3] *Professeur titulaire de Chimie organique à la Faculté des Sciences.*

[4] *Chargé de cours en Chimie générale à la Faculté des Sciences.*

Partie théorique

L'insolubilisation progressive des semicarbazones du glucose que nous avons déjà indiquée (2) aurait constitué la clef de la méthode que nous nous proposons d'élaborer, sans une insolubilisation à peu près proportionnelle des semicarbazides elles-mêmes. En effet, il est nécessaire pour permettre aux semicarbazides substituées de se dissoudre en présence de la solution aqueuse du sucre, d'additionner celle-ci d'alcool ou d'un solvant approprié. Cette addition a pour effet de retenir en même temps une quantité appréciable de semicarbazone; lorsque celle-ci se forme et demeure en solution, un équilibre chimique s'établit entre la semicarbazide et la semicarbazone et il empêche la réaction d'être totale. Il n'est pas possible non plus, dans ces conditions, d'évaluer directement la quantité de glucose-semicarbazone qui s'est formée parce qu'elle ne précipite pas intégralement.

On peut cependant modifier les conditions de la réaction de façon à obtenir quand même un rendement quantitatif de glucose-semicarbazone; on peut théoriquement y arriver si on élimine l'eau produite au cours de la réaction, afin de supprimer l'équilibre. Il importe toutefois de noter que le glucose à doser se trouve inévitablement en solution aqueuse; l'eau de cette solution devra donc être éliminée en même temps que celle qui est fournie par la réaction.

Le problème de l'élimination de l'eau des systèmes en équilibre présente plusieurs solutions; on peut, par exemple, lui substituer un solvant moins volatil et soumettre le mélange réactionnel à la distillation ou à une simple évaporation. Des essais préliminaires au moyen de la *p*-nitrophényl-4-semicarbazide nous avaient en effet montré que l'addition de quantités croissantes d'alcool absolu à une solution aqueuse de glucose fournit des rendements de glucose-semicarbazone qui se rapprochent de plus en plus du rendement théorique. Le diagramme suivant correspond à cinq condensations pour lesquelles la concentration de l'eau a varié de 6 à 75%, du fait de l'addition

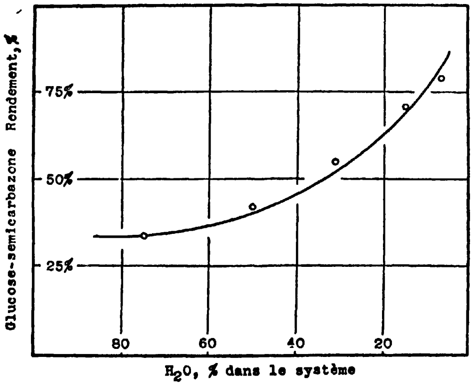


FIG. 1.

d'alcool; le rendement de glucose-semicarbazone a par le fait même augmenté de 33 à 78% du rendement théorique. L'allure de la courbe confirme l'hypothèse théorique, c'est-à-dire que l'élimination complète de l'eau du système, au fur et à mesure de sa formation, conduira éventuellement à un rendement quantitatif de glucose-semicarbazone:

$$\mathrm{CH_2OH{-}(CHOH)_4{-}CHO + \underset{\alpha}{NH_2}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2} \longrightarrow$$

$$\longrightarrow \mathrm{H_2O + CH_2OH{-}(CHOH)_4{-}CH{=}\underset{\alpha}{N}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2}$$

Pour l'élimination de l'eau du système en équilibre, nous avons substitué l'alcool amylique à l'éthanol; il bout à 132° C. et permet ainsi une élimination rapide de l'eau par évaporation; d'autre part, il dissout bien la *p*-nitrophényl-4-semicarbazide et sa glucose-semicarbazone.

Dans ces nouvelles conditions, la glucose-semicarbazone ne peut plus précipiter, et il nous faut disposer d'une méthode qui permette de la doser facilement, en présence de la semicarbazide libre qui l'accompagne inévitablement. Cette méthode consiste à ajouter au mélange un léger excès de *m*-nitrobenzaldéhyde; ce réactif précipite quantitativement à froid la *p*-nitrophényl-4-semicarbazide sans affecter la glucose-semicarbazone correspondante. En outre, la *m*-nitrobenzal-semicarbazone qui se forme est très peu soluble même dans les milieux alcooliques additionnés d'alcool amylique.

Il suffit donc de filtrer la solution qui a été additionnée de *m*-nitrobenzaldéhyde pour la débarrasser de la *p*-nitrophényl-4-semicarbazide libre qu'elle contient. En chauffant maintenant le filtrat après l'avoir acidifié légèrement, on obtient l'hydrolyse de la glucose-semicarbazone; cette hydrolyse libère de la *p*-nitrophényl-4-semicarbazide qui se combine aussitôt à son tour à la *m*-nitrobenzaldéhyde pour donner un nouveau précipité de *m*-nitrobenzal-*p*-nitrophényl-4-semicarbazone insoluble; le poids de cette semicarbazone correspond à celui de la glucose-semicarbazone et, par extension à celui du glucose lui-même:—

$$\mathrm{CH_2OH{-}(CHOH)_4{-}CH{=}\underset{\alpha}{N}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2 + H_2O} \longrightarrow$$

$$\longrightarrow \mathrm{CH_2OH{-}(CHOH)_4{-}CHO + \underset{\alpha}{NH_2}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2}$$

$$\mathrm{NO_2C_6H_4{-}CHO + \underset{\alpha}{NH_2}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2} \longrightarrow$$

$$\longrightarrow \mathrm{NO_2C_6H_4CH{=}\underset{\alpha}{N}{-}\underset{\beta}{NH}{-}\underset{\gamma}{CO}{-}\underset{\delta}{NH}{-}C_6H_4NO_2 + H_2O}$$

Les rapports arithmétiques entre les poids moléculaires des substances qui figurent dans ces deux équations indiquent que 180.1 g. de glucose correspondent à la formation de 358.2 g. de glucose-semicarbazone puis à la précipitation de 329.2 g. de semicarbazone de la *m*-nitrobenzaldéhyde. Le poids de glucose qui est passé à l'état de semicarbazone au cours d'une condensation peut dès lors être calculé en multipliant par 0.5471 (180.1/329.2) le poids de *m*-nitrobenzal-semicarbazone que l'on recueille.

Méthode et résultats

Pour le dosage expérimental du glucose par la *p*-nitrophényl-4-semicarbazide, nous avons adopté la méthode suivante qui est basée sur les données théoriques précédentes: à 10 cm.^{3} de solution de glucose, contenant de 0.02 à 0.1 g. de ce sucre, on ajoute une quantité de *p*-nitrophényl-4-semicarbazide qui est à peu près proportionnelle à la quantité de glucose, déterminée approximativement par un essai préliminaire (0.1 g. de semicarbazide si la quantité de glucose est voisine de 0.02 ou 0.03 g.; 0.2 g. de semicarbazide si le glucose atteint 0.05 g. environ; ou 0.3 g. de semicarbazide si l'on a jusqu'à 0.1 g. de sucre). On y mélange 20 cm.^{3} d'alcool amylique et 1 cm.^{3} de solution à 10% d'acide orthophosphorique puis on porte au bain-marie bouillant. L'emploi d'acide phosphorique est justifié par les travaux d'Ardagh et Rutherford (1), qui ont démontré la propriété catalytique supérieure de l'acide phosphorique pour l'obtention des hydrazones et des combinaisons analogues.

Pour faciliter l'élimination rapide de l'eau et assurer en même temps l'homogénéité du milieu, on ajoute au mélange 40 cm.^{3} d'alcool éthylique absolu. Lorsque le volume est réduit par évaporation à 12 ou 15 cm.^{3}, ce qui prend environ 45 min., l'eau est depuis quelque temps déjà totalement éliminée et la condensation du glucose est complète. On retire du bain, on ajoute 5 cm.^{3} d'alcool absolu et on refroidit rapidement jusqu'à 22° à 25° C.

On procède alors à l'élimination de l'excès de *p*-nitrophényl-4-semicarbazide en ajoutant 5 cm.^{3} d'eau et 5 cm.^{3} de solution alcoolique à 10% de *m*-nitrobenzaldéhyde; la précipitation de la semicarbazone s'amorce immédiatement et peut être considérée complète au bout d'une heure et quarante minutes à la température de 22° à 25° C. Après filtration, la solution ne contient plus que la glucose-*p*-nitrophényl-4-semicarbazone en présence d'un excès de *m*-nitrobenzaldéhyde; on dose le glucose combiné en ajoutant à la solution, quatre gouttes d'acide chlorhydrique concentré et en la portant sur bain-marie pendant encore 30 min. Il se produit rapidement un deuxième précipité de *m*-nitrobenzal-*p*-nitrophényl-4-semicarbazone, en belles aiguilles soyeuses; on recueille sur entonnoir taré et on lave à l'eau puis on sèche à l'étuve pendant une heure à 105° à 110° (0.20 g. de *m*-nitrobenzal-semicarbazone laissés 48 h. à cette température n'ont accusé aucun changement de poids).

Le poids du précipité recueilli multiplié par le facteur 0.5471 correspond au poids de glucose présent dans la solution originale.

Cette méthode, appliquée d'abord à des solutions pures de glucose (Dextrose anhydre, échantillon No 41 du Bureau des Standards, Washington) a donné les résultats présentés au Tableau I.

Le protocole qui vient d'être exposé peut être modifié pour permettre d'atteindre des concentrations en glucose inférieures à celles qui figurent au Tableau I. Lorsque la concentration en glucose est inférieure à 0.20%, on peut prendre 50 cm.^{3} de solution sucrée, y ajouter 100 cm.^{3} d'alcool absolu et les autres solvants ou réactifs, dans les proportions qui ont déjà été indiquées;

TABLEAU I

Dosage expérimental du glucose par la *p*-nitrophényl-4-semicarbazide

No	Glucose pesé, g.	Volume de solution, cm.³	Conc. du glucose, %	Semicarbazone recueillie, g.	Glucose trouvé, g.	Moyenne
1	0.1000	10	1.00	0.1835	0.1001	0.10006
2	0.1000	10	1.00	0.1840	0.1005	
3	0.1000	10	1.00	0.1826	0.0999	
4	0.1000	10	1.00	0.1830	0.1000	
5	0.1000	10	1.00	0.1832	0.1001	
6	0.1000	10	1.00	0.1837	0.1003	
7	0.1000	10	1.00	0.1815	0.0993	
8	0.0700	10	0.70	0.1269	0.0693	
9	0.0500	10	0.50	0.0955	0.0522	0.0513
10	0.0500	10	0.50	0.0933	0.0512	
11	0.0500	10	0.50	0.0912	0.0498	
12	0.0500	10	0.50	0.0950	0.0520	
13	0.0200	10	0.20	0.0369	0.0202	0.0208
14	0.0200	10	0.20	0.0407	0.0222	
15	0.0200	10	0.20	0.0373	0.0204	
16	0.0200	10	0.20	0.0376	0.0205	

on évapore jusqu'à volume final de 12 ou 15 cm.³ et on procède comme dans la méthode générale. Voici les résultats qui ont été ainsi obtenus:

TABLEAU II

Dosage du glucose en solution à 0.1% par la *p*-nitrophényl-4-semicarbazide

No	Glucose pesé, g.	Volume de solution, cm.³	Conc. du glucose, %	Semicarbazone recueillie, g.	Glucose trouvé, g.	Moyenne
17	0.0500	50	0.10	0.0950	0.0519	0.0510
18	0.0500	50	0.10	0.0952	0.0520	
19	0.0500	50	0.10	0.0904	0.0494	

Enfin, la méthode a été mise à l'essai, sans défécation préalable, sur des solutions de glucose contenant des substances réductrices, ou sur des urines dont le titre en glucose avait été déterminé au Fehling, en utilisant le ferrocyanure de potassium comme indicateur.

Discussion

La méthode qui vient d'être décrite est essentiellement expérimentale et elle est loin d'être définitive; elle se propose seulement de démontrer la possibilité d'appliquer la réaction bien définie des semicarbazides avec les aldéhydes et les cétones à une détermination quantitative du glucose.

TABLEAU III

DOSAGE DU GLUCOSE EN SOLUTION RÉDUCTRICE PAR LA *p*-NITROPHÉNYL-4-SEMICARBAZIDE

No	Nature de la solution	Pourcentage de glucose	Semicarbazone recueillie, g.	Glucose trouvé, %
20	Solution pure	0.542*	0.0967	0.529
21	Solution pure	0.546*	0.1009	0.552
22	Saturée d'acide urique	0.546*	0.0991	0.542
23	Urine diabétique	0.358**	0.0676	0.370
24	Urine diabétique	1.627**	0.2980	1.656
25	Urine diabétique	0.281**	0.0513	0.272

* *Titre déterminé par pesée du glucose avant dissolution.*
** *Titre déterminé au Fehling avec ferrocyanure.*

Il importe cependant de préciser quelles en sont les limites. On peut d'abord se demander si une solubilité de quelques milligrammes seulement de la *m*-nitrobenzal-*p*-nitrophényl-4-semicarbazone ne pourrait pas avoir, par le jeu des dilutions et des relations arithmétiques du calcul, une influence qui, rapportée au glucose, constitue une erreur appréciable. Le mécanisme même des précipitations empêche cette erreur de se produire: en effet, lors de la première précipitation, celle qui a pour but d'éliminer l'excès de semicarbazide, la *m*-nitrobenzal-semicarbazone a complètement précipité, sauf la petite quantité qui correspond à sa solubilité dans le milieu. Celui-ci se trouve ainsi saturé. La deuxième précipitation fournit une nouvelle quantité de cette semicarbazone, dans un milieu dont les propriétés dissolvantes sont demeurées sensiblement les mêmes; cette nouvelle quantité de semicarbazone précipite donc intégralement, puisque le milieu en était déjà saturé, et son poids correspond avec exactitude à la quantité de glucose-semicarbazone hydrolysée, et par extension, il correspond aussi au poids de glucose présent dans le milieu initial.

La principale limite de la méthode provient de la concurrence qui s'établit entre la fin de précipitation de l'excès de semicarbazide et le commencement de l'hydrolyse de la glucose-semicarbazone; cette hydrolyse a tendance à commencer avant même que la semicarbazide libre n'ait eu le temps de précipiter complètement à l'état de semicarbazone insoluble. De telle sorte que le temps le plus favorable pour cette précipitation (une heure et quarante minutes) correspond probablement au moment où il y a superposition des deux phénomènes avec compensation mutuelle.

Si on contrôle avec soin la durée de cette précipitation, les résultats sont assez précis et uniformes. Mais si on laisse prolonger ce temps au-delà de celui qui a été indiqué, le résultat devient rapidement déficitaire par suite de la disparition d'une partie de la glucose-semicarbazone; ce temps, prolongé à deux heures et demie, conduit à un déficit de 4%. Si au contraire, on abrège le temps offert à la précipitation, le résultat en glucose devient trop fort par suite de l'élimination incomplète de l'excès de semicarbazide; au cours de l'hydrolyse subséquente de la glucose-semicarbazone, ce résidu de semicarbazide s'ajoute à celle qui provient de l'hydrolyse et conduit ainsi à un résultat trop élevé. Un temps de précipitation de 60 min. seulement a donné un résultat en glucose excédant de 4% le résultat théorique.

La température peut avoir aussi une influence sur la valeur du résultat si elle subit des variations considérables; mais les variations ordinaires de la température du laboratoire (22° à 25°) n'ont pas une influence appréciable.

Bibliographie

1. ARDAGH, E. G. R. et RUTHERFORD, F. C. J. Am. Chem. Soc. 57(6) : 1085-1088. 1935.
2. BARRÉ, R. et PICHÉ, L. Can. J. Research, B, 20(2) : 17-20. 1942.

EFFECT OF INITIAL DRYING TEMPERATURE ON THE APPARENT LIGNIN CONTENT OF PLANT TISSUES[1]

By D. MacDougall[2] and W. A. DeLong[3]

Abstract

A study of the effect of initial drying temperature on the apparent lignin content of various succulent plant tissues has been made. Air-drying, drying *in vacuo* at 60° C., air-drying after removal of constituents soluble in cold water and in cold dilute ethanol, and oven-drying at 105° C. have been compared.

Drying of immature or succulent tissues at 105° C. results in a markedly higher apparent lignin content (as determined by the 72% sulphuric acid method) than is obtained after drying under the other conditions specified. This difference may be of especial importance when it is desired to compare the lignin contents of tissues of different degrees of maturity, or which have received different treatments, as in comparison of ensiled with non-ensiled materials.

The nitrogen and methoxyl contents of the lignin preparations isolated indicate that drying at 105° C. results in the inclusion of nitrogenous or carbohydrate materials, or both, in the lignin fraction. Evidence that the interfering substances are mainly easily soluble and removable prior to desiccation was obtained. It is indicated that non-lignin methoxyl may be present in lignin preparations prepared from tissues dried at 105° C.

At present there is no general agreement among plant chemists as to the temperature at which succulent tissues should be dried prior to the determination of their lignin content. The official A.O.A.C. method (1, p. 143) involves preliminary drying of the tissue at 105° C. Various investigators (9, 10, 11, 12) have employed lower temperatures. A review of the literature indicates, however, that lignin determinations are most frequently made on tissues that have been dried at 100° to 105° C. in air. Nevertheless, there is considerable evidence that suggests that drying at such an elevated temperature is likely to be productive of error. Thus Campbell and Booth (2, 3) found that oven-drying resulted in an increase in the apparent lignin content of both soft and hard woods. At the same time there was a corresponding decrease in furfuraldehyde-yielding material suggestive of condensation of the latter with lignin.

Waksman and Iyer (15) report experiments in which protein was added to lignin preparations. They maintain that formation of a ligno-protein took place and that the resistance of such a complex to microbial decomposition was rendered greater by drying and by an elevated temperature of formation. It seems probable that similar complexes may be formed in succulent tissues on drying at an elevated temperature, or, if such are previously formed, they may at least be rendered more resistant to subsequent decomposition.

---

[1] *Manuscript received November 28, 1941.*

Contribution from the Faculty of Agriculture of McGill University, Macdonald College, Que. From part of a thesis by D. MacDougall in partial fulfilment of the requirements for the degree of Master of Science. Macdonald College Journal Series No. 169.

[2] *Holder of a bursary under the National Research Council of Canada 1940-41.*

[3] *Assistant Professor of Chemistry.*

Wagner (14) carried out drying experiments on leaves of fodder beets, sweet fodder beets, and sugar beets. He dried samples of these tissues at 60° C. and at 105° to 110° C. and found that the digestibility of the protein was considerably reduced; this was particularly true in regard to the material dried at the higher temperature. It is possible that this effect was due to condensation of protein with lignin to form an indigestible complex.

With the object of obtaining further information on the effect of the conditions of the drying of plant tissues on their apparent lignin content the following materials have been analyzed; Swede turnips (roots), young winter rye (leaves), silage prepared from young winter rye, rhubarb (petioles), and garden beets (roots). The preparation of these materials for analysis is described below.

A. Preparation of Material

Turnip

Only the central part of turnip roots (free from brown heart) was used. The portion of the tissue outside the xylem was removed. The tissues thus selected were ground in a food chopper through a plate with holes of 9 mm. diameter. The ground tissue from several turnips was mixed, and 500-gm. portions were weighed out for drying. Samples I and II were dried at 105° C. in an electric air-oven; I*a* and II*a* were dried in the vacuum oven at 60° at an average pressure of 25 to 28 in. of mercury. The dried tissue was ground in a Wiley mill to pass a screen with circular openings of 0.5 mm. diameter.

Turnip samples Nos. I and I*a* were taken from freshly harvested roots, whereas II and II*a* were from roots that had been kept in cellar-storage for approximately six weeks.

Winter Rye

The rye was sown in the early part of August and harvested at the end of October.

Representative samples of the young plants were taken for analysis at the time the crop was ensiled. These were prepared in the same way as turnip samples Nos. I and I*a*, i.e., (i) oven-dried, and (ii) vacuum-dried at 60° C. The samples to be oven-dried were in this case placed in wire-bottomed trays and then put into a large oven where a current of hot air was drawn up through them. The temperature of drying was 103° C.

Winter Rye Silage

The silos were filled about the end of October, 1940, and the samples for analysis were taken during the last week of March, 1941. Silo I (Samples I, I*a*) was filled with rye plants only. In the case of Silo II, phosphoric acid was added to the rye plants in sufficient quantity to give a 4% concentration. Samples from each of these silos were dried both at 103° C. in the hot air oven (I, II) and at room temperature by being spread out on the desk top (I*b*, II*b*). All samples were then ground in a Wiley mill to pass a 0.5 mm. screen. The oven-dried material was redried at 105° C. and portions of the air-dry samples were also dried at this temperature to determine their residual moisture content. The residue remaining after pretreatment* of the oven-dried material was redried at 105° C., while that from the air-dried material was dried *in vacuo* at 60° C., before the final lignin determinations were carried out.

Rhubarb

The rhubarb was gathered early in the morning. Only stalks of fairly uniform age were used. The leaves and the bases of the petioles were removed and the stalks were carefully washed to remove all sand and other adhering material. The excess moisture from washing was allowed to dry off at room temperature. The stalks were arranged according to size and the same number of stalks from the various size groups were put into each of three samples. These were then weighed.

Sample I was cut into transverse sections of about one-quarter inch in length and dried to constant weight in the air-oven at 105° C. The dried tissue was then ground in a Wiley mill to pass the 0.5 mm. sieve.

Samples II and II*a* were cut into small pieces and shredded with water in a Model B "Waring Blender"†. For each batch of cut tissue 200 ml. of water was first put into the shredder and rhubarb added in very thin slices until the mixture was too viscous to allow efficient shredding.

The material was then transferred to 250-ml. centrifuge bottles for separation of the solid phase. It was found that adding 25 ml. of 95% alcohol to the mixture in each bottle so as to give approximately a 10% alcohol mixture facilitated the settling out of the solid material. The mixture was centrifuged for 10 min. at an approximate speed of 2500 r.p.m., and the supernatant liquid was then siphoned off. The residues were combined and recentrifuged. Water was used to rinse out the centrifuge bottles when combining the residues. The procedure was repeated until the sample was reduced to the smallest possible volume. Approximately 1500 ml. of water was used for the washing and transferring of a kilogram of fresh tissue. This extraction with water and 10% alcohol was carried out at room temperature.

The residual material of both Samples II and II*a* was next covered with 95% alcohol, well stirred, and centrifuged again. The supernatant alcohol was then siphoned off. Sample II was transferred to a large evaporating dish by means of a little more 95% alcohol. The latter was removed by heating on the steam bath, and drying was completed in the air-oven at 105° C. Sample II*a* was transferred to a large Büchner funnel with 95% alcohol and dried by suction at the pump. It was then placed in a small rotary air-drier. This was composed of a cylindrical can on a steel shaft. A pulley was fixed on one end of the shaft so that the can could be turned by means of an electric motor. The ends of the can were removed and replaced by 60-mesh wire gauze. The sample was placed in the can and a current of air was blown through it by means of an electric fan placed at one end.

---

* *Pretreatment for removal of substances interfering in the lignin determination; see Section B—Methods of Analysis—for details.*

† *Manufactured by Waring Corporation, New York City.*

After six hours in the drier the sample was removed and broken up into very fine pieces and returned to the apparatus for completion of the drying process, which took about eighteen hours. Finally, the sample was finely ground and a portion was dried in the oven at 105° C. to determine its residual moisture content. After pretreatment these samples were again dried in the air-drier prior to determination of their lignin content.

Beets

Fresh beets were gathered on the mornings of July 3 and July 18. They were washed with water and the tops and long tapering ends of the tap roots were removed. On each date the beets were arranged according to size and divided into two portions. The average weight per beet of the four samples was: I—39.2 gm., I*a*—41.1 gm., II—88.5 gm., and II*a*—87.2 gm. Samples I and I*a* were collected on July 3, II and II*a* on July 18.

Samples (I, II) were weighed, sliced into large evaporating dishes, and placed in the air-oven at 105° C. to dry. Samples I*a* and II*a* were shredded in the "Waring Blender" in the same way as the rhubarb. In this case it was found necessary to add alcohol for the second as well as for the first centrifuging. Each sample was concentrated into four 250 ml. centrifuge bottles and then transferred to a large Büchner funnel. Approximately three litres of water were used for the shredding and transferring of one kilogram of fresh material. The residues were next washed with 95% alcohol until the filtrates were nearly colourless. After removing as much alcohol as possible at the pump, the material was transferred to the rotary drier for completion of the drying process at room temperature. After pretreatment these samples were redried in the air-drier prior to lignin determination. The moisture content of the air-dried pretreated beet and rhubarb tissues was low, being of the order of 8%.

B. Methods of Analysis

Lignin Determinations

It was decided to determine the lignin content of the various tissues by the 72% sulphuric acid method, as this procedure has been most widely used by earlier workers. All the tissues were pretreated by extracting with alcohol-benzene, hot water, and 1% hydrochloric acid solution as prescribed in the official A.O.A.C. method (1, p. 143).

The extracted and dried samples were ground in an iron mortar to pass a 40-mesh sieve. The ground material was dried to constant weight at the appropriate temperature (60°, 105° C., etc.) and the actual lignin determinations were carried out exactly as described by Manning and DeLong (6). It was found that if the sample was allowed to stand for one-half to one hour after refluxing with 3% sulphuric acid, filtration was facilitated. The residues were filtered on asbestos in ignited Gooch crucibles.

To aid filtration, diatomaceous earth was added to the acid mixture and a layer was also placed over the asbestos in the crucible. The filter-aid was ignited for half an hour in the muffle furnace before being used. The residual lignin was thoroughly washed with hot water and the Gooch crucibles were dried at 105° C., weighed, ignited in the muffle furnace at a dull red heat for half an hour, and reweighed. The loss in weight on ignition was taken as the weight of ash-free lignin obtained from the original sample.

Nitrogen Determinations

Samples for nitrogen determinations were filtered in the same way as described above except that the ignited crucibles and diatomaceous earth were dried at 105° C. both before and after filtering. The increase in weight represented the amount of crude lignin in the original material.

The percentages of nitrogen and methoxyl are both calculated on crude lignin. It was not possible to make a correction for ash content, as the amount of ash found in various lignin preparations from the same material was somewhat variable. However, the ash content of the lignin isolated from turnip, rhubarb, and beet samples was almost negligible, and thus there is very little error from this source in the nitrogen and methoxyl values for these substances. On the other hand, lignin isolated from fresh rye and rye silage contained from 5 to 10% ash, and therefore the nitrogen and methoxyl values found for these materials are somewhat low.

In washing the residues for nitrogen determinations care was taken to leave no lignin particles adhering to the inner walls of the crucibles, from which they could be removed only with difficulty when dry. The entire contents of the crucibles was transferred to 500-ml. Kjeldahl flasks and rinsed down with distilled water. The digestion mixture consisted of 4 gm. of potassium sulphate, 1 gm. of mercuric acetate, and 15 ml. of concentrated c.p. sulphuric acid. After digesting to a small volume, the inner walls of the flasks were washed down with distilled water, a 5 ml. portion of concentrated sulphuric acid was added, and digestion was continued for half an hour after the mixture had become colourless. The digest was cooled, filtered into a 100 ml. volumetric flask, and diluted to volume. Ten-ml. portions of this solution were used in the micro-distillation apparatus. The distillation was carried out as described by Pregl (13).

Methoxyl Determinations

Samples for methoxyl determinations were filtered on sintered glass crucibles of porosity G 2 and G 3. Naphthalene was used to speed filtering as suggested by Mueller and Herrmann (7). After filtration the naphthalene was sublimed on the hot water-bath and the residual lignin was then dried in the usual manner and weighed. The lignin filtered in this way was very easily removed from the crucibles, and any possible contamination of the sample due to particles of glass scraped from the crucible in removing the lignin was avoided. The methoxyl determinations were carried out according to the Vieboch and Schwappach modification of the Ziesel method as described by Clark (4). The hydriodic acid used in these determinations was prepared according to the method described by Clark (5).

Results and Discussion

The lignin values in Table I are expressed as percentage of ash-free lignin in oven-dry material. In the case of the rhubarb and beet samples, which were extracted before drying, the percentage dry weight was calculated from the dry weight of the samples dried at 105° C. Portions of the material dried at low temperatures were subsequently dried at 105° C., so that their lignin contents could be calculated on an oven-dry-weight basis.

TABLE I

THE EFFECT OF TEMPERATURE OF PRELIMINARY DRYING ON THE APPARENT LIGNIN CONTENT OF VARIOUS PLANT TISSUES

Material	Sample	Loss in dry weight in pretreatment, %	Ash-free lignin, dry weight basis, %	Nitrogen in crude lignin, %	Methoxyl in crude lignin, %	Remarks
Turnip	I*	84.2	6.27 ± 0.07 (3)‡	6.68	0.406	Newly harvested roots
	I_a†	90.0	1.31 ± 0.02 (3)			
	II	88.7	4.84 ± 0.09 (3)	4.26	0.968	Roots kept in cellar-storage for about six weeks
	II_a	92.6	1.13 ± 0.04 (3)	8.50	1.43	
Young rye	I	70.6	6.08 ± 0.23 (3)	6.46	1.69	Fresh material
	I_a	76.8	4.28 ± 0.01 (3)	4.79	2.21	
Silage	I	67.3	8.86 ± 0.04 (3)	6.98	1.61	Silage made from young rye
	I_b	73.0	4.06 ± 0.08 (3)	4.21	1.53	
	II	70.7	7.86 ± 0.09 (6)	5.57	1.51	Rye silage + 4% phosphoric acid
	II_b	73.0	4.20 ± 0.07 (6)	3.46	1.83	
Rhubarb	I	70.1	13.6 ± 0.2 (3)	3.95	0.705	Fresh rhubarb
	II	82.4	2.74 ± 0.02 (3)	5.36	2.88	Fresh rhubarb from which soluble materials were washed before drying
	II_c	82.5	1.73 ± 0.03 (3)	3.65	5.53	
Beets	I	86.6	2.82 ± 0.15 (3)	8.16	1.13	Beets harvested July 3
	I_c	93.5	0.550 ± 0.014 (3)	5.48	3.14	
	II	84.2	6.34 ± 0.25 (3)	5.84	0.541	Beets harvested July 18
	II_c	92.9	0.554 ± 0.02 (3)	6.79	2.61	

* *Sample numbers without subscript letters indicate that the samples were dried at 100° to 105° C.*

† *Samples marked (a) were dried in vacuo at 60° C.; those marked (b) were air-dried at room temperature; and those marked (c) were air-dried at room temperature after their easily soluble materials had been washed out with cold water and dilute alcohol.*

‡ *The percentage of lignin is followed by the average deviation and, in parentheses, the number of determinations carried out.*

The data of Table I show clearly that the temperature of preliminary drying has a marked effect on the apparent lignin content of the tissues analysed. In every case the apparent lignin content of samples dried at a low temperature is much lower than that of samples of the same tissue dried at an elevated temperature. This result may probably be ascribed to formation of artifacts and to a greater condensation of nitrogenous and carbohydrate materials with the lignin at the higher temperatures. It is also possible that drying at high temperatures caused a change in the molecular constitution of the lignin itself and rendered it more insoluble in the reagents used for the pretreatments and lignin determinations. Of these two possibilities the former seems the more probable and has considerable experimental evidence in its favour (8, p. 153). However, it may be that a part of the fraction which some workers have called "soluble" lignin is being determined in the oven-dried material but not in that dried at room temperature. Evidence in support of such a hypothesis is difficult to obtain, since accurate determination of small amounts of "soluble" lignin in the pretreatment extracts, accompanied as they are by considerable quantities of carbohydrates and nitrogenous materials, is not practicable at present.

In any event, the nitrogen and methoxyl contents of the isolated lignin would seem to indicate that the interference avoided by low temperature drying is much greater than any error likely to be caused by solution of lignin.

In every tissue studied, the absolute amount of nitrogen in the residue from material dried at elevated temperatures was much greater than from tissue dried at low temperatures. In some instances there was 8 or 10 times as much nitrogen in the residue from the oven-dried sample as in that from the material dried at low temperature. In no case was the absolute amount of methoxyl as great in the "low temperature" lignin as in the other, although the percentage was usually higher in the former. This may be due to condensation of methoxyl-containing carbohydrates, probably of a hemicellulosic nature, with the lignin on drying at elevated temperatures. That the lignin from material dried at a low temperature is purer than that from material dried at elevated temperatures is indicated by the fact that the absolute amount of nitrogen in the former was always much lower and the percentage of methoxyl usually higher. As indicated above, however, the nitrogen content is probably the safer criterion of purity.

Comparison of the results for rhubarb samples Nos. I and II would seem to indicate that it is the easily soluble plant constituents that cause the bulk of the interference in material dried at high temperatures. The only difference between the treatments given to Samples I and II was that the latter had its easily soluble constituents washed out with water and approximately 10% alcohol prior to drying at 105° C. Yet, Sample I had almost five times as much apparent lignin as Sample II. The interference in Sample I is, perhaps, largely due to formation of humin-like substances from easily soluble carbohydrate and nitrogenous materials. On the other hand, comparison of rhubarb samples Nos. II and II*c* shows that the whole interference is not caused by readily soluble materials. Both samples had their readily soluble constituents removed prior to drying, then Sample II was dried at 105° C. and Sample II*c* at room temperature. Sample II showed an apparent lignin content of 2.74% while Sample II*c* had only 1.73% lignin. These results indicate that the main interference in the determination of the lignin content of succulent tissues dried at high temperatures is due to formation of humin-like substances from readily soluble plant constituents. There is also a smaller but still significant interference due to water insoluble material.

The hypothesis suggested to explain the results obtained in the analysis of the rhubarb samples is supported by a comparison of the percentages of dry weight lost by the samples dried at high and at low temperatures in the pretreatment extractions with alcohol-benzene, hot water, and 1% hydrochloric acid. Such a comparison shows that in every instance more material was removed from the tissue dried at low temperature. However, the differences in amount lost by pretreatment are often slight and never proportional to the lowering of the apparent lignin content of the material. It would seem that high temperature drying renders a part of the readily soluble plant constituents insoluble in both the pretreatment solvents and in the concentrated acid, especially the latter. On the other hand, although the readily soluble constituents of the samples dried at low temperature appear to be rendered virtually insoluble in alcohol-benzene, hot water, and dilute hydrochloric acid, they, as well as more difficultly soluble substances, can still be removed by the concentrated acid treatment or by the hydrolysis with dilute acid which follows it.

The fact that the apparent lignin content of material dried at low temperatures shows very little variation with changes in the nature of the other plant constituents would seem to indicate that probably a relatively pure substance is being isolated. Changes in the composition of beet roots with increasing age and of Swede turnip roots on storing have a marked effect on the amount of lignin residue obtained from oven-dried samples of these tissues, but have little or no effect on the amount of lignin obtained from samples dried at a low temperature.

A comparison of the results for fresh rye and rye silage when both were dried at 100° to 105° C. indicates that ensiling causes a marked increase in lignin as percentage of dry weight. However, during the ensiling period there was a loss of approximately 16.8% of the original dry weight from both silos. This loss is presumably due almost entirely to decomposition of readily soluble carbohydrates. If it is assumed that there was no loss of lignin during the ensiling period, then, on the basis of the values obtained for fresh material, we would expect to obtain 7.31% lignin in the silage. The actual values obtained were significantly higher than the expected, viz., 8.86 and 7.86%, and it would thus appear that high temperature drying caused an even greater error with the silage than with the fresh material.

If samples are dried at low temperatures the apparent effect of ensiling seems to be to lower the lignin content of young rye. Based on the results for fresh material, the silage should contain approximately 5.14% lignin when dried at low temperature. The actual results, 4.06 and 4.20%, were much lower than the expected. This discrepancy may be due to the fact that the fresh material was vacuum-dried at 60° C., whereas the silage samples were air-dried at room temperature before the lignin determinations were carried out. Thus the results on these materials cannot be compared and it would appear that drying at 60° C. results in the inclusion of some non-lignin material with the lignin fraction. Further investigation of this point is necessary.

References

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 5th ed. A.O.A.C., Washington, D.C. 1940.
2. Campbell, W. G. and Booth, J. Biochem. J. 24 (3) : 641-648. 1930.
3. Campbell, W. G. and Booth, J. Biochem. J. 25 (3) : 756-762. 1931.
4. Clark, E. P. J. Assoc. Official Agr. Chem. 15 (1) : 136-140. 1932.
5. Clark, E. P. Ind. Eng. Chem Anal. Ed. 10 (12) : 677. 1938.
6. Manning, K. R. and DeLong, W. A. Sci. Agr. 22 (2) : 69-79. 1941.
7. Mueller, W. J. and Herrmann, W. Tech.-Wiss. Teil, Papierfabr. 24 : 185. 1926. *Abstracted in* Chem. Abstracts, 20 (16) : 2746. 1926.
8. Norman, A. G. The biochemistry of cellulose, the polyuronides, lignin, etc. Oxford University Press, New York and London. 1937.
9. Peterson, C. J. and Hixon, R. M. Ind. Eng. Chem. Anal. Ed. 1 (2) : 65-67. 1929.
10. Peterson, C. J., Walde, A. W., and Hixon, R. M. Ind. Eng. Chem. Anal. Ed. 4 (2) : 216-217. 1932.
11. Phillips, M., Goss, M. J., Davis, B. L., and Stevens, H. J Agr. Research, 59 (5) : 319-366. 1939.
12. Platenius, H. Plant Physiol. 9 (3) : 671-680. 1934.
13. Pregl, F. Quantitative organic microanalysis. 3rd English ed. J. & A. Churchill, Ltd., London. 1937.
14. Wagner, H. Landw. Z. 40 : 441; Z. Ver. deut. Zuckerind. 71 : 251. 1921. *Abstracted in* Chem. Abstracts, 15 (15) : 2519. 1921.
15. Waksman, S. A. and Iyer, K. R. N. Soil Sci. 36 (1) : 69-82. 1933.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXXI. *CORYDALIS MONTANA* (ENGELM.) BRITTON[1]

By Richard H. F. Manske[2]

Abstract

Seven known alkaloids have been isolated from *Corydalis montana* (Engelm.) Britton, namely: protopine, *dl*-tetrahydro-palmatine, corydaline, capauridine, capaurine, scoulerine, and capaurimine. Two new bases have been isolated. One of these, alkaloid F57, was obtained by reduction of a quaternary base which itself could not be obtained crystalline. *C. aurea* has also yielded the same base. It is represented by $C_{18}H_{21}O_4N$ containing three methoxyls. The second new base, alkaloid F56, is represented by $C_{23}H_{27}O_6N$ containing four methoxyl groups.

It is pointed out that the chemical differences between *C. aurea* and *C. montana* are of sufficient magnitude to allocate specific rank to each plant.

Corydalis montana (Engelm.) Britton is so closely related to *C. aurea* Willd. that it was classed as variety *occidentalis* of the latter by Engelmann. The habits of the plants and the morphology of their flowers are so similar that only critical examination by a competent botanist can serve to authenticate a series of specimens. The writer is therefore particularly grateful to Dr. H. A. Senn, Botanist, Department of Agriculture, Ottawa, who, in collaboration with Dr. G. H. M. Lawrence of the Bailey Hortorium, Cornell University, Ithaca, N.Y., undertook such an examination. They consider it a good species distinct from *C. aurea* Willd. Specimens are deposited in the herbarium of the Bailey Hortorium and in the herbarium of the Division of Botany and Plant Pathology, Department of Agriculture, Ottawa.

Because of lack of material it was not possible to subject *C. montana* to as thorough an examination as in the case of *C. aurea*. It was nevertheless possible to isolate a total of nine alkaloids, six of which, namely, protopine, *dl*-tetrahydro-palmatine, capaurine, capauridine, corydaline, and a new base, F57, are now known to occur in *C. aurea* (1, 3). Two of the remaining three, namely, capaurimine and scoulerine, had previously been isolated from *C. pallida* (4) and *C. scouleri* (2) respectively. The last, alkaloid F56, was obtained only in very small amounts so that it could not be characterized apart from its analyses, which yielded figures in good agreement with $C_{23}H_{27}O_6N$ containing four methoxyl groups.

It is pertinent to point out that the chemical examination had been completed before the plant had been properly identified, although it had been tentatively regarded as *C. montana*. On chemical grounds alone it now seems reasonable to allocate to it specific rather than varietal rank.

---

[1] *Manuscript received February 2, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1044.

[2] *Chemist.*

Experimental

The material for the present investigation was grown in a local garden from seed which came from a single plant. When dried and ground it weighed 9.0 kilos.

The following is a summary of the various fractions and the contained alkaloids.

Base hydrochlorides extracted from aqueous solution by means of chloroform,

BC—Non-phenolic bases,—*dl*-tetrahydro-palmatine, corydaline.
EC—Phenolic bases extracted from alkaline solution by means of ether,—alkaloid F56.
BCE + EEC—Phenolic bases precipitated by carbon dioxide,—capaurine, capauridine.
CEC—Phenolic bases not precipitated by carbon dioxide but extracted by means of chloroform,—alkaloid F57.

Base hydrochlorides not extracted from aqueous solution by means of chloroform,

BS—Non-phenolic bases,—protopine.
BSE+EES—Phenolic bases precipitated by carbon dioxide,—scoulerine, capaurimine.

dl-Tetrahydro-palmatine and Corydaline

The main fraction of the alkaloid separated as the sparingly soluble hydrochloride when the acidic solution was extracted with ether prior to basification. The free base was regenerated and recrystallized from methanol. It then melted at 150° C.*, either alone or in admixture with an authentic specimen of *dl*-tetrahydro-palmatine. The yield was 0.04%.

The bases from the more soluble hydrochlorides were extracted from the basified solution with ether. The residue in contact with methanol yielded a small amount of protopine. It was therefore redissolved in dilute hydrochloric acid and the solution extracted with chloroform to eliminate the BS bases. The residue from the chloroform extract was redissolved in water, the filtered solution basified with ammonia, and the bases were extracted with ether. The residue from the extract crystallized readily in contact with methanol. The base was recrystallized from hot methanol, and it then consisted of the characteristic stout tablets of corydaline melting at 136° C. either alone or in admixture with an authentic specimen. Yield, 0.01%.

Alkaloid F56

The fraction EC deposited a very sparingly soluble base which, after washing with methanol, melted indefinitely at 196° C. It was recrystallized twice from chloroform-methanol, and it then melted at 207° C. In admixture with capauridine, which it resembles in appearance and which occurs in this fraction, it was completely liquid at 190° C. Its solution in sulphuric acid is pale olive in colour which merely changes to brown on heating. The analytical figures agree best with $C_{23}H_{27}O_6N$ containing four methoxyl groups. Calcd. for $C_{23}H_{27}O_6N$: C, 66.83; H, 6.54; N, 3.39; 4 OMe, 30.04%. Found: C, 67.12, 66.94; H, 6.49, 6.70; N, 3.44, 3.12; OMe, 29.96%.

* *All melting points are corrected.*

Capauridine and Capaurine

The fractions BCE and EEC in contact with methanol deposited a small amount of base which was recrystallized from chloroform-methanol. It melted at 207° C. and admixture with a specimen of capauridine did not lower the melting point. Yield, 0.003%.

The bases from the mother liquor from the capauridine as well as the totally phenolic fraction of EC were dissolved in dilute acid, the bases regenerated from the filtered solution, and extracted with ether. The extract was evaporated to a small volume and treated with just sufficient methanol to redissolve the resin that had separated. The base which then crystallized was recrystallized first from methanol-ether and then from methanol. It was obtained in stout prisms that melted at 164° C. either alone or in admixture with capaurine. Yield, 0.003%.

Alkaloid F57

The aqueous carbonated solution from which ether extraction has removed fraction EEC is in general free of organic bases. In the case of some plants, however, extraction with chloroform removes a not inappreciable amount of base. *C. aurea* and the plant under consideration yielded a comparatively large amount of a water soluble uncrystallizable resin. The dark golden colour suggested that a substantial amount of protoberberine bases might be present. The residues from the two different plants were therefore subjected to reduction with zinc dust in dilute acetic acid in parallel experiments until the colour had faded to a pale yellow. The cooled and filtered solutions were basified with ammonia and extracted with ether. The residues in contact with methanol crystallized readily and yielded the same base melting at 127° C. It was recrystallized from hot methanol in which it is only moderately soluble. The colourless prisms thus obtained melted sharply at 129° C. and proved to be non-phenolic. This base, alkaloid F57, is best represented by $C_{18}H_{21}O_3N$ containing three methoxyl groups. Calcd. for $C_{18}H_{21}O_3N$: C, 72.24; H, 7.02; N, 4.68; 3 OMe, 31.10%; mol. wt. 299. Found: C, 71.58, 71.82; H, 7.31, 7.38; N, 4.51, 4.24; OMe, 32.48%; mol. wt. 338.

Protopine

The fraction BS yielded no base other than protopine, which was readily obtained in a state of high purity; m.p. 210° C. The yield was 0.07%.

Scoulerine and Capaurimine

Neither fraction BSE nor EES deposited a crystalline base in contact with methanol. They were combined, dissolved in dilute hydrochloric acid, the bases regenerated from the filtered solution, and extracted with ether. The residue from the ether solution was neutralized in methanol with anhydrous hydrogen chloride, and the somewhat concentrated solution treated with ethyl acetate until the incipient turbidity just disappeared on mixing. In the course of several days a crystalline hydrochloride separated. The addition of ethyl acetate was continued from day to day until no further crystalline product was obtained. It was filtered off and washed with methanol–ethyl-acetate. As thus obtained, the hydrochloride consisted of a mixture, one component of which was virtually insoluble in cold water and the other readily soluble. The less soluble hydrochloride when shaken with ammonia and ether yielded several milligrams of a base that melted not quite sharply at 200° C. This melting point was not depressed when the base was mixed with a specimen of scoulerine from *C. scouleri*.

The base regenerated from the more soluble hydrochloride crystallized from ether, and when repeatedly recrystallized from methanol-ether it melted at 213° C. A further small amount of this base was obtained from the methanol–ethyl-acetate, another liquor from which the hydrochlorides had been obtained. This base in admixture with a specimen of capaurimine from *C. pallida* melted at 212° C. A methoxyl determination yielded 27.07%. Three methoxyls in $C_{20}H_{23}O_5N$ require 26.05%.

References

1. Manske, R. H. F. Can. J. Research, 9(11) : 436-442. 1933.
2. Manske, R. H. F. Can. J. Research, B, 14(10) : 347-353. 1936.
3. Manske, R. H. F. Can. J. Research, B, 16(3) : 81-90. 1938.
4. Manske, R. H. F. Can. J. Research, B, 18(3) : 80-83. 1940.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. APRIL, 1942 NUMBER 4

THE ALKALOIDS OF PAPAVERACEOUS PLANTS

XXXII. *STYLOPHORUM DIPHYLLUM* (MICHX.) NUTT., *DICRANOSTIGMA FRANCHETIANUM* (PRAIN) FEDDE AND *GLAUCIUM SERPIERI* HELDR.[1]

BY RICHARD H. F. MANSKE[2]

Abstract

The only alkaloids found in *Stylophorum diphyllum* and in *Dicranostigma franchetianum* were protopine, chelidonine, and stylopine. It is concluded that there is no chemical justification for allocating separate generic rank to these plants. *Glaucium serpieri* yielded protopine, glaucine, isocorydine, and aurotensine. Luteanine, present in *G. flavum*, could not be found. In addition there was present a small amount of phenolic base which on methylation yielded sinactine. It is concluded that the plant probably deserves specific rather than varietal rank.

The alkaloids of *Stylophorum diphyllum* (Michx.) Nutt. were isolated in 1901 by Schlotterbeck and Watkins (6) who reported the presence of protopine, chelidonine, sanguinarine, stylopine, and diphylline. In a previous communication (4) the author pointed out that stylopine is $C_{19}H_{17}O_4N$ and not $C_{19}H_{19}O_5N$ as reported by the authors already quoted. The *dl*-form is identical with bis-methylenedioxy-tetrahydro-protoberberine and melts at 221° C.*, whereas the *l*-form melts at 202° C. The author has previously recorded the occurrence of the *dl*-form (1) and a mixture, not separated, of the *l*- and *dl*-forms (2, 4). It is probable that diphylline is in fact *dl*-stylopine, although no trace of it has been found in this investigation. Sanguinarine as known in 1901 was inadequately characterized and has since been shown to consist of at least two bases, the more readily obtainable of which is chelerythrine. During the examination of another plant, the author has had occasion to isolate and characterize chelerythrine but it could not be found in *S. diphyllum*. The yellow colour of the sap of the plant is not due to a coloured alkaloid but to a mixture of highly oxygenated compounds which, however, were not obtained pure. The genus *Dicranostigma* as now recognized comprises three species, all native to Asia. It was at one time regarded as *Stylophorum*. The species now reported upon, *D. franchetianum* (Prain) Fedde, was found to contain only three alkaloids and the same three only were obtained from *S. diphyllum*, namely, protopine, chelidonine, and stylopine. The only chemical difference was that the last alkaloid was present in the

---

[1] *Manuscript received February 5, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1050.

[2] *Chemist.*

* *All melting points are corrected.*

dl-form. It would appear from this observation that the chemical constituents so characteristic of the species in the subfamily Fumarioideae are not necessarily of the same degree of specificity in other genera or species. Nevertheless it is concluded that, in view of the chemical similarity between the two plants, there is no adequate justification for their separation into two genera.

In this connection an examination of *Glaucium serpieri* Heldr. is of interest. This plant is frequently regarded as a variety of *G. flavum* Crantz., namely var. *serpieri* Halaczy. It was found that the two plants each contained the following alkaloids,—protopine, glaucine, isocorydine, and aurotensine. The presence of luteanine (3) in *G. serpieri* could, however, not be demonstrated. There was obtained a small amount of an amorphous base which on methylation with diazomethane yielded an alkaloid identical with a partly racemic sinactine, first obtained from *Fumaria officinalis* (1). It appears therefore that the phenolic precursor is either cheilanthifoline (5) or an isomer. It is not likely that such a base was overlooked in the previous exhaustive examination of *G. flavum*.

Experimental

There was available for these investigations the following amounts of dried and ground material—*S. diphyllum*—4.0 kg. (roots); *D. franchetianum*—8.65 kg.; and *G. serpieri*—4.82 kg. All material was grown in a local garden. The *Stylophorum* was collected in autumn when the plants were dormant, and the following record refers only to the roots although the leaves collected in summer were also examined. They contained only very small amounts of the same bases. The other plant material was collected during the flowering period before any seed had ripened.

The procedure adopted in the three cases was the same and followed that repeatedly used by the author.

Protopine and Chelidonine

Protopine and chelidonine occur together in the non-phenolic fraction (BS) (hydrochlorides not extracted from aqueous solution by means of chloroform). The protopine from *G. serpieri* was readily obtained in a pure condition and the presence of other bases, except in traces, is improbable.

The separation of protopine and chelidonine can be easily effected by the following procedure, which is almost quantitative and was here employed. The dried mixture of bases is dissolved in hot methanol and the filtered solution inoculated with a crystal of protopine. The chelidonine is readily soluble in methanol and the protopine which crystallizes may be further purified via its hydrobromide or by direct crystallization from chloroform-methanol. It was present to the extent of about 0.03% in both *S. diphyllum* and *D. franchetianum*.

The methanolic mother liquor from the protopine is acidified with dilute hydrochloric acid, the methanol boiled off, and the filtered solution allowed to cool. The sparingly soluble hydrochloride of chelidonine then crystallizes. It is preferably recrystallized once from hot water and the free base is then regenerated by adding an excess of ammonia to a rapidly cooled aqueous solution of the salt. The washed and dried precipitate is dissolved in methanol and the solution evaporated to a thin syrup. An excess of dry ether is added, the resulting turbid solution filtered, and the filtrate evaporated to a small volume. Seeding with a crystal induces immediate crystallization of stout highly refracting prisms of chelidonine, which melt at 135 to 136° C. The maximum melting point of 137° C. is attained by one recrystallization. The yield was 0.02% from *D. franchetianum* and 0.05% from *S. diphyllum.* In admixture with an authentic specimen of chelidonine, prepared from *Chelidonium majus* L. by the same procedure, the alkaloid obtained from the above sources showed no depression in melting points.

Stylopine

The non-phenolic fractions (BC) from the *Stylophorum* and the *Dicranostigma* yielded sparingly soluble hydrochlorides from which the free bases were regenerated. They were then recrystallized from hot methanol. The former yielded *l*-stylopine melting at 202° C. The latter yielded the less soluble *dl*-stylopine melting at 221° C. either alone or in admixture with a specimen of *dl*-stylopine from *F. officinalis* (1). The mother liquors in this case yielded a less pure base melting at 206° C., which proved to be identical with the partly racemic stylopine obtained from *C. claviculata* (4).

The presence of phenolic bases in these two plants could not be demonstrated.

Glaucine

The glaucine was isolated as in the case of *G. flavum* (3). Exhaustive examination of the mother liquors failed to yield luteanine, and other bases were absent except in possible traces.

Isocorydine

The phenolic fraction (EC) was freed of contaminating non-phenolic bases by redissolving in dilute acid and adding an excess of potassium hydroxide. The filtêred aqueous solution was saturated with carbon dioxide and extracted with ether. The washed ethereal solution was evaporated to a small volume, filtered to remove a turbidity, and concentrated to a thin syrup, which almost immediately deposited colourless stout prisms of isocorydine. The base melted at 185° C. either alone or in admixture with an authentic specimen of isocorydine. The yield was 0.004%.

Aurotensine

The combined phenolic fractions (BSE and EES) were obtained by extracting the carbonated solution with ether. The residue from the ether extract crystallized readily in contact with a small volume of methanol. The characteristic plates thus obtained melted at 128° C., and this melting point was not lowered when the base was admixed with a specimen of aurotensine. The yield was about 0.002%, including a small amount recovered from the mother liquor as hydrochloride.

There remained a small amount of alkaloid that could not be obtained crystalline either as free base or as hydrochloride. It was methylated with diazomethane and the non-phenolic base converted to its hydrochloride, which was sparingly soluble in water or methanol. The regenerated base was recrystallized from methanol, and it then consisted of colourless fine needles melting sharply at 117° C. In admixture with a specimen of sinactine from *F. officinalis*, it melted at the same temperature.

References

1. Manske, R. H. F. Can. J. Research, B, 16(12) : 438-444. 1938.
2. Manske, R. H. F. Can. J. Research, B, 17(3) : 89-94. 1939.
3. Manske, R. H. F. Can. J. Research, B, 17(12) : 399-403. 1939.
4. Manske, R. H. F. Can. J. Research, B, 18(4) : 97-99. 1940.
5. Manske, R. H. F. Can. J. Research, B, 18(4) : 100-102. 1940.
6. Schlotterbeck, J. O. and Watkins, H. C. Ber. 35 : 7-23. 1902.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXXIII. *CORYDALIS CHEILANTHEIFOLIA* HEMSL.[1]

By Richard H. F. Manske[2]

Abstract

Corydalis cheilantheifolia Hemsl. was found to contain the following alkaloids,—*l*-canadine, stylopine, *l*-corypalmine, *l*-cheilanthifoline, protopine, and allocryptopine. It is pointed out that the presence of these alkaloids is evidence of the close relation of this plant to *C. ophiocarpa*. Incidently, further proof for the constitution of ophiocarpine, previously given, has been obtained by oxidation to a corydaldine.

Corydalis cheilantheifolia Hemsl. (*C. daucifolia* Léveillé et Vaniot), as its name indicates, is the fern-leaved *Corydalis* (from *Cheilanthes* Sw., a genus of ferns). It is botanically related to *C. ophiocarpa*, being placed in the same subsection, and indeed its natural habitat overlaps that of the latter. It is native to China in the provinces of Hupeh, Szechwan, and Kweichow.

The chemical constituents resemble most closely those of *C. ophiocarpa* Hook. f. et Thoms. (3). The following alkaloids are common to both plants,—protopine, allo-cryptopine, *l*-canadine, berberine, *l*-corypalmine, and *l*-stylopine (previously reported as alkaloid F40). In addition to these alkaloids, *C. cheilantheifolia* contains cheilanthifoline (4), *dl*-stylopine, and a non-basic nitrogenous substance which yields analytical figures in fair agreement with $C_{21}H_{18}O_8N_2$. Ophiocarpine, an alkaloid thus far obtained only from *C. ophiocarpa*, could not be isolated from the plant under discussion. The correctness of the constitution of this alkaloid as previously given (3) was confirmed by the simple expedient of oxidizing it with permanganate to 6 : 7-methylenedioxy-1-keto-1 : 2 : 3 : 4-tetrahydro-isoquinoline. This is proof that the hydroxyl group cannot be in positions 5 or 6.

Experimental

The material was grown in a local garden and consisted almost entirely of the first year's growth. The plant is a facultative biennial but not entirely winter hardy in this locality. There was available a total of 8.6 kg. of which the roots constituted only 0.4 kg. Considerable difficulty was encountered in obtaining satisfactory separation and purification of the alkaloids, and it is probable that the examination of a larger amount of material will disclose the presence of a number of other alkaloids.

The following is a summary of the various fractions and the contained alkaloids.

---

[1] *Manuscript received February 7, 1942.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1051.

[2] *Chemist.*

Base hydrochlorides extracted from aqueous solution by means of chloroform:—

BC—Non-phenolic bases,—*l*-canadine, *l*- and *dl*-stylopine.

BCE + EEC—Phenolic bases,—*l*-corypalmine, cheilanthifoline.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, allo-cryptopine.

BSE + EES—Phenolic bases,—(not crystallized).

l-Canadine and Berberine

The non-phenolic base mixture (BC) was redissolved in a large volume of dilute hydrochloric acid and the filtered solution cooled. The sparingly soluble salt that separated was recrystallized from hot water. It was then dissolved in hot water and the rapidly cooled solution basified with ammonia. The precipitated base was recrystallized from hot methanol; it then melted, either alone or in admixture with a specimen of *l*-canadine, at 135° C.* $[\alpha]_D^{22} -317°$ (c = 0.4 in methanol).

The ammoniacal filtrate from the canadine was acidified with acetic acid and heated with zinc dust until the yellow colour had faded. The addition of ammonia and extraction with ether yielded a base which when recrystallized from methanol melted sharply at 170° C. Its identity with *dl*-canadine was proved by a mixed melting point determination, and therefore the ammonia soluble base was berberine.

dl- and l-Stylopine

The mother liquor from the crystallization of the canadine and berberine hydrochlorides was basified with ammonia and the precipitated bases were washed thoroughly with water to remove the remaining quaternary salts. The dried product was recrystallized a number of times from methanol. There was ultimately obtained a base that proved to be identical with a specimen of *dl*-stylopine (5) melting at 220° C.

The more soluble fractions were reconverted to hydrochlorides and these recrystallized from hot water. A small amount of *l*-canadine hydrochloride was first obtained. The more soluble but crystallized salt was converted to free base, which was extracted with hot methanol. The less soluble portion consisted substantially of *dl*-stylopine. The extract on slight concentration and cooling deposited colourless fragile needles melting at 196° C. In admixture with a specimen of alkaloid F40 from *C. ophiocarpa* it melted at the same temperature. Found: C, 70.15, 70.45; H, 5.43, 5.38; N, 4.91, 4.90%. Calc. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.26; N, 4.33%.

Further crystallization did not materially increase the melting point, but in admixture with a specimen of *l*-stylopine from *Stylophorum diphyllum* (5) it melted indefinitely at 200° C. It was positively characterized as stylopine by conversion to the *dl*-form melting at 221° C. This was accomplished by the usual procedure of oxidation first with alcoholic iodine and subsequent reduction with zinc and acetic acid.

---

* *All melting points are corrected.*

l-Corypalmine and l-Cheilanthifoline

The fractions (EEC and BCE) and the completely phenolic component of (EC) in contact with methanol crystallized readily. When recrystallized from chloroform-methanol it melted at 230° C. and at the same temperature in admixture with specimens of *l*-corypalmine from other sources.

The methanolic mother liquor from which the above base had been crystallized was evaporated to a small volume and treated with methanolic hydrogen chloride. The sparingly soluble salt which separated was washed with acetone and converted to free base by treating in aqueous solution with ammonia. The base, *l*-cheilanthifoline, crystallized readily from hot methanol and melted at 184° C. Further crystallization did not raise the melting point. It proved to be identical with the same base obtained from *C. scouleri* (1) and *C. sibirica* (2). Yield, 20 p.p.m.

Protopine and Allo-cryptopine

The fraction (BS) was dissolved in chloroform, the solution was filtered and evaporated, and the residue dissolved in hot methanol. The addition of a crystal of protopine induced the immediate crystallization of the same alkaloid. It was readily obtained pure by recrystallization from chloroform-methanol (m.p. 210° C.). The yield of protopine was 0.14% from the aerial portion and 0.74% from the roots, the latter figure being almost as high as the corresponding one for *C. sibirica*.

The combined mother liquors were evaporated to a small volume and a further small amount of protopine crystallized out. Some methanol was added and the solution filtered with the aid of charcoal. The addition of a crystal of allo-cryptopine induced immediate crystallization of this base. It was obtained pure by recrystallization from hot methanol, which served to eliminate a small amount of protopine still present. The yield of allo-cryptopine (m.p. 160° C.) was about 0.06%.

Neutral Nitrogenous Substance

The methanolic extract of the roots was treated with dilute hydrochloric acid and the insoluble portion filtered off. The filtrate deposited a crust of yellow crystalline material in the course of several days. It was filtered off, washed with warm water, and recrystallized from much boiling water. It was then washed with methanol, in which it is virtually insoluble, and recrystallized once more from hot water. As thus obtained it consisted of dark brown glistening prisms, which neither melted nor showed any evidence of decomposition at 360° C. It contained neither halogen nor methoxyl and was virtually ash free. Found: C, 58.99, 58.95; H, 4.19, 4.07; N, 6.53, 6.55%. Calc. for $C_{21}H_{18}O_8N_2$: C, 59.12; H, 4.23; N, 6.58%.

Oxidation of Ophiocarpine

A solution of the base (0.5 gm.) in 50 cc. of water containing a drop of hydrochloric acid was neutralized to incipient turbidity with sodium carbonate and treated with a cooled aqueous solution of potassium permanganate (0.9 gm.). When the last had been reduced, a pellet of potassium hydroxide was added, and the heated solution filtered. It was cooled and extracted with ether. The residue from the ether was boiled with a little water, the solution cooled, filtered, and extracted with ether. The residue from this extract was sublimed *in vacuo* and thus obtained in brilliant colourless prisms melting at 183° C. In admixture with a specimen of 6 : 7-methylenedioxy-1-keto-1 : 2 : 3 : 4-tetrahydro-isoquinoline similarly prepared from canadine it melted at the same temperature.

References

1. MANSKE, R. H. F. Can. J. Research, B, 14(10) : 347-353. 1936.
2. MANSKE, R. H. F. Can. J. Research, B, 14(10) : 354-359. 1936.
3. MANSKE, R. H. F. Can. J. Research, B, 17(2) : 51-56. 1939.
4. MANSKE, R. H. F. Can. J. Research, B, 18(4) : 100-102. 1940.
5. MANSKE, R. H. F. Can. J. Research, B, 20(3) : 49-52. 1942.

COLUMN PACKING AND THE SEPARATION OF ISOTOPES[1]

By H. G. Thode[2] and F. O. Walkling[3]

Abstract

An expanded shale aggregate packing material for fractionating columns has been investigated. The new packing is inert, cheap, and easily wetted by water. Columns packed with this material have been tested in the distillation of hydrocarbons and with water systems. The results indicate that the new packing compares favourably, both with regard to efficiency and throughput, with other column packings and is more efficient with water systems. It should have industrial applications as well as applications in the separation of isotopes.

Introduction

For the past two years the writers have been interested in developing a cheap and efficient column packing for use in the separation of isotopes by distillation and chemical exchange methods. During the course of this work a column packing has been investigated which seems to have applications in columns of large diameter for the separation of isotopes. This packing material is cheap, compares favourably with other packings in the separation of hydrocarbons and is particularly efficient with water systems, probably owing to its exceptional wetting properties. Because this new packing may have applications in the separation of isotopes and also because a cheap and efficient packing may have wide application in industrial processes this report of the preliminary investigations is presented.

Columns using stainless steel gauze (6) and aluminum turnings (4) have been used in the separation of oxygen isotopes by the distillation of water, but have not given good results. The Pegram rotating column (2) was more effective but has other disadvantages. The writers have used a 60 ft. column 1 in. in diameter, packed with 5 mm. glass helices, obtaining a 3.5-fold change in the ratio of oxygen isotopes. However, the results were disappointing in view of the high efficiencies obtained when the columns are used for the separation of hydrocarbons. In order to produce larger quantities and higher concentrations of the O^{18} isotope, larger columns are required using the cascade system of Thode and Urey (7). In this system, concentrated material from a column of larger diameter is fed into a column of smaller diameter. It is for these columns of larger diameter that a very efficient and cheap packing is required, as their large volume makes the cost of the more expensive type of packing prohibitive.

---

[1] *Manuscript received January 5, 1942.*

Contribution from the Chemistry Department, McMaster University, Hamilton, Ont., with financial assistance from the National Research Council of Canada.

[2] *Assistant Professor of Chemistry.*

[3] *Graduate student.*

Experimental and Results

The packing material was prepared by the Cooksville Co. from a special shale*. Crushed shale is passed through a furnace at 2700° F., which is well above the melting point of the shale. Carbon dioxide is formed owing to the presence of small amounts of carbonates, and an expanded clinker is produced. These clinkers are then crushed, cleaned, and graded according to particle size. The resulting aggregates are used as packing in the columns. The irregular shape of the aggregate particles prevents close packing, and the honeycomb surface results in a large surface area. The approximate chemical composition is given in Table I. The calcium, magnesium, and iron are probably present as monosilicates, which would account for the exceedingly low chemical activity of the packing.

TABLE I

CHEMICAL ANALYSIS OF SHALE AGGREGATE PACKING, %

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	Loss on ignition
64.12	21.34	8.20	3.10	2.60	0.45	0.15

The columns packed with shale aggregate have been tested on three different systems; carbon-tetrachloride–benzene, the distillation of water, and a chemical exchange process. In all cases the columns were packed by pouring the loose material into the top of the column so that it fell at random. In the apparatus used for the first two systems, the column was insulated with two layers of heavy asbestos paper and two layers of crumpled aluminum foil; the auxiliary equipment, boiler, condenser, etc., were of standard design. Provision was made for the removal of samples from each end of the column.

Carbon-tetrachloride–benzene

At the start of each run a sufficient quantity of carbon-tetrachloride–benzene mixture was introduced into the boiler by pouring the liquid through the top of the column. This procedure was followed to ensure complete wetting of the packing. The mixture was then boiled at a constant rate with total reflux of vapour at the top. Samples were removed from the column every 30 min. and were analysed by the refractive index method, data from the International Critical Tables being used (3, p. 77). This procedure was continued until the analysis indicated that the column had reached a steady state. The concentration range used was so chosen as to obtain the most accurate plate efficiency data.

Several runs were made with each packing. The results obtained with glass helices, carborundum, corundum and five different grades of shale aggregate packings are given in Table II. The number of theoretical plates in Column 7 was determined graphically by means of the equilibrium data of

---

* *Dundas shale, used by the Cooksville Company for the manufacture of "Haydite" aggregate.*

Rosanoff and Easley (5, p. 971) for carbon-tetrachloride–benzene mixtures. The H.E.T.P. (height equivalent to a theoretical plate) is obtained by dividing the length of the column by the number of theoretical plates.

TABLE II

COMPARISON OF VARIOUS TYPES OF COLUMN PACKING ON HYDROCARBONS

Packing		Free space, %	Rate of flow, litres/hr.	Mole % CCl_4		Total theoretical plates	H.E.T.P., cm. (in.)
Type	Grade			Top	Bottom		
Shale aggregate	2–3 mesh	52.2	1.36	45.3 44.5	12.3 11.8	12.0 12.0	8.3 (3.3) 8.3 (3.3)
Shale aggregate	4–6 mesh	53.8	1.26	55.8 57.2	6.5 7.6	20.0 19.5	5.0 (2.0) 5.0 (2.0)
Shale aggregate	6–8 mesh	55.6	1.14	66.5 63.6	9.3 7.3	24.0 23.5	4.2 (1.7) 4.3 (1.7)
Shale aggregate	8–10 mesh	—	1.20 0.60	65.3 67.3	7.3 6.1	24.5 26.7	4.1 (1.6) 3.8 (1.5)
Shale aggregate	10–12 mesh	—	1.00	67.8 59.2	9.8 6.1	24.7 22.2	4.0 (1.6) 4.1 (1.8)
Glass helices	5 mm. × .5 mm.	80.	—	54.6 48.0	10.6 9.8	16.5 15.2	6.1 (2.4) 6.6 (2.6)
Carborundum	10 mesh	—	0.84	44.5 47.2	2.2 3.6	20.5 19.5	4.9 (1.9) 5.1 (2.0)
Corundum	8 mesh	47.	—	36.0	7.3	12.7	7.9 (3.1)

Column 40 in. long, I.D. 1.5 in. Operated under total reflux.

The shale aggregate is very efficient and compares favourably with the glass helix packing developed by Fenske. Optimum efficiency is obtained with the 8–10 mesh grade of aggregate packing. However, coarser packing can be used without much loss in efficiency, with the advantage of a lower resistance to vapour flow. The back pressure of a 1 in. column 60 ft. long packed with 3–4 mesh shale aggregate was the same as a similar column packed with 5 mm. glass helices. The columns were operated on the distillation of water with a pressure of 5 cm. of mercury at the top and a rate of flow of 3.8 cc. per min. giving a back pressure of 10 cm. In some processes the throughput of the column will be limited not by the flooding velocities (which are relatively high) but by the maximum permissible back pressure. There is little change in efficiency with increase in column diameter from 1.5 to 3 in. (see Table III). Fenske reports similar results with columns packed with glass helices.

TABLE III

VARIATION OF EFFICIENCY OF SHALE AGGREGATE PACKING WITH COLUMN DIAMETER

(Tests on 4–10 mesh packing)

Carbon-tetrachloride–benzene system

Inside diameter of column, in.	Rate of flow litres/hr.	Mole % CCl_4		No. of theoretical plates	H.E.T.P., cm. (in.)
		Top	Bottom		
1.5	0.5	60.4	6.7	23.3	4.4 (1.7)
2.84	3.0	54.8	6.4	19.4	5.2 (2.1)
2.84	3.0	61.6	6.6	22.2	4.6 (1.8)

H_2O^{16} – H_2O^{18} system

Inside diameter of column, in.	Rate of flow, litres/hr.	Mole % H_2O^{18}		No. of theoretical plates	H.E.T.P., cm. (in.)
		Top	Bottom		
1.5	0.3	.178	.206	48.8	2.1 (.83)
2.84	1.5	.192	.222	48.5	2.2 (.86)

Columns 40 in. long. Operated under total reflux.

Distillation of Water

In the distillation of water, as in the separation of carbon tetrachloride and benzene, the apparatus was operated under total reflux with a large reservoir of liquid in the boiler, until a steady state was reached. Water samples were removed from the top and bottom of the column. By the method of Cohn and Urey (1) these samples were brought to isotopic equilibrium with carbon dioxide, which was then analysed with a mass spectrometer. The mole fraction of O^{18} as determined by this method is accurate to ±1%. The number of theoretical plates, k, in the column at equilibrium and operating under total reflux is defined by the equation:

$$\frac{\dfrac{n}{1-n}}{\dfrac{N}{1-N}} = \alpha^k, \tag{1}$$

where N and n are the mole fractions of O^{18} at the top and bottom of the column respectively, and α is the simple process separation factor.

Two tests have been made with the columns packed with shale aggregate. The results are given in Table III. In calculating the number of theoretical plates, α was taken as 1.003 at 100° C., a value obtained experimentally by Wahl and Urey (9).

The results are very encouraging and indicate that the new packing is very efficient in the separation of the oxygen isotopes by the distillation of water. As in the hydrocarbon runs, the 3 in. column is as efficient as the 1.5 in. column. The liquid holdup per unit length was found to be about double that of the columns packed with glass helices. However, the indications are that the holdup per plate will be less in the columns of larger diameter. More extensive tests are now in progress.

Chemical Exchange Process

The chemical exchange process used by H. C. Urey and his co-workers for the separation of the nitrogen isotopes (7) has been discussed in detail. The process depends on an exchange between ammonium nitrate solution and ammonia gas. A 60% solution (by weight) of ammonium nitrate is pumped into the top of a fractioning column, *F*, at a constant rate (Fig. 1). This solution

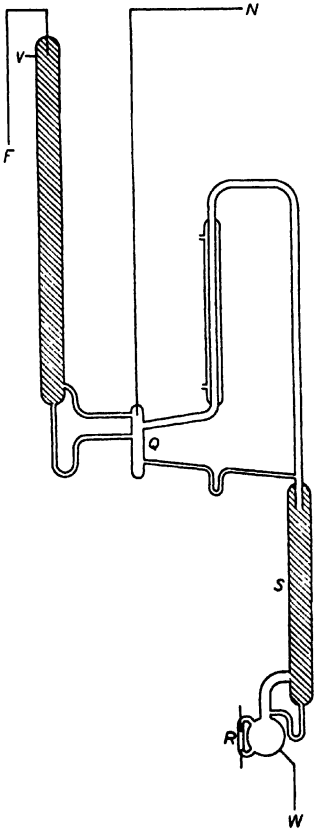


FIG. 1. *Chemical exchange apparatus.*

TABLE IV

COMPARISON OF VARIOUS TYPES OF COLUMN PACKING ON CHEMICAL EXCHANGE

Packing	Length, cm.	I.D., cm.	Rate of flow, cc./min.	N^{15} enrichment factor	No. of theoretical plates	H.E.T.P., cm. (in.)	Holdup per plate, cc.
Stedman stainless steel gauze	92.0	2.5	2.5	1.18	7.2	12.7 (4.8)	5.0
Stedman stainless steel gauze	92.0	2.5	2.5	1.17	6.9	13.3 (5.2)	5.0
Glass helices, 5 mm.	120.0	1.0	0.65	1.42	15.3	7.8 (3.3)	—
Glass helices, 6 mm.	130.0	2.2	2.5	1.29	11.2	11.6 (4.6)	4.1
Glass helices, 6 mm.	130.0	2.2	6.3 10.0*	1.31	11.8	11.0 (4.3)	4.1
Berl saddles, 6 mm.	130.0	2.2	5.0	1.19	7.6	17.1 (6.7)	6.6
Berl saddles, 6 mm.	170.0	7.0	50.0	1.22	8.7	19.6 (7.6)	—
Berl saddles, 6 mm.	170.0	7.0	80.0	1.24	9.4	18.1 (7.1)	—
Shale aggregate, 3 mm.	100.0	2.5	6.5 11.0*	1.46	16.6	6.0 (2.4)	5.4

* *Flooding velocity.*

drains to the foot of the column to the reaction chamber, Q, where alkali is added, N, to liberate the ammonia. The ammonia is then stripped from the waste solution by means of the stripper, S, and boiler, R, returning to the column where it flows to the top, counter current to the solution and escapes to a stripper and vacuum pump at, V. Since N^{15} is favoured in the liquid phase there is a net transport of N^{15} toward the foot of the column, where it concentrates. The apparatus is operated at a pressure of 10 cm. of mercury and at room temperature. For this system the number of theoretical plates, k, in a column at equilibrium and operating at total reflux is defined by Equation (1), where N and n are the mole fractions of N^{15} at the top and bottom of the column, respectively.

This process calls for a large number of theoretical plates, as α differs only slightly from unity (approximately 1.023) (8). Also, owing to the low initial concentration and the low rate of transport, columns with a small holdup must be used. Those with a large number of theoretical plates may require several months to reach a steady state even when they have a low holdup. However, by using a cascade system of columns such that a column of small diameter operates on concentrated material from a column of larger diameter, the time required to reach a given concentration can be reduced. It is for these columns of relatively large diameter that a cheap and efficient packing material is especially required. Since the nitrogen process is typical of chemical exchange processes involving water solutions, the writers have used it to test columns packed with shale aggregate. The results in Table IV include for comparison unpublished data of one of the authors obtained in the Chemistry Department of Columbia University.

The shale aggregate packing is more efficient than the other packings tested. It is almost twice as efficient as the Fenske helices or the Stedman wire gauze packing. The liquid holdup per plate is about the same for all the columns tested, being slightly less for columns packed with glass helices. However, the efficiency varies by a factor of three for the different packings. With regard to throughput, the shale aggregate columns compare favourably with the glass helix columns. Both have high flooding velocities. The back pressure is higher in the aggregate columns. However, the higher efficiency of the aggregate will partly compensate for this, as shorter columns can be used. Further, it should be mentioned that the vapour velocity in most chemical exchange processes is limited by the solubility of gas or salt and the back pressure may be negligible. The results indicate that the new packing has application in chemical exchange processes where water solutions are used.

Discussion

The expanded shale aggregate has a large surface area on which liquids, including water, spread easily. This wetting property of the aggregate is due in part to the chemical, and in part to the physical, nature of the surface. A thin film of water is absorbed on the packing. This film can be removed by a stream of dry air. Although this absorbed liquid adds to the holdup of a packed column, it prevents a film of grease from forming and makes complete wetting of the packing possible under most conditions. The high efficiency of the shale aggregate packing with water systems is due in part to this factor. The efficient wetting of the packing also reduces channelling of the liquid and makes possible much higher flooding velocities.

The shale aggregate has several advantages over other cheap aggregate packings such as carborundum and corundum. It is very light weight and is easily supported in a column. It has a higher percentage of free space; this means a lower back pressure and a higher throughput. Towers 12 ft. in diameter and up to 300 ft. in length are used in the industry both for hydrocarbon and water systems. The high towers are required because of the low efficiency of the cheap packing materials available. It may be that with cheap aggregate packing available in small sizes much shorter columns could be used.

The packing was developed primarily for the further concentration of O^{18} by the distillation of water. A three stage cascade system has been designed and is now under construction.

Acknowledgments

The writers wish to thank Mr. Alfred Miles for help in chemical exchange experiments, and Mr. E. T. Clarke for his suggestions and interest in the problem. Finally, thanks are due to Prof. David Rittenberg of the Columbia Medical Centre, New York, who analysed some of the samples with his mass spectrometer.

References

1. Cohn, M. and Urey, H. C. J. Am. Chem. Soc. 60(3) : 679-687. 1938.
2. Huffman, J. R. and Urey, H. C. Ind. Eng. Chem. 29(5) : 531-535. 1937.
3. International Critical Tables. Vol. 7. McGraw-Hill Book Company, Inc., New York and London. 1930.
4. Randall, M. and Webb, W. A. Ind. Eng. Chem. 31 : 227-230. 1939.
5. Rosanoff, M. A. and Easley, C. W. J. Am. Chem. Soc. 31(9) : 953-987. 1909.
6. Stedman, D. F. Can. J. Research, B, 13(2) : 114-121. 1935.
7. Thode, H. G. and Urey, H. C. J. Chem. Phys. 7(1) : 34-39. 1939.
8. Urey, H. C., Huffman, J. R., Thode, H. G., and Fox, M. J. Chem. Phys. 5 : 856-868. 1937.
9. Wahl, M. H. and Urey, H. C. J. Chem. Phys. 3 : 411-414. 1935.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. MAY, 1942 NUMBER 5

NOTE ON THE PYROLYSIS OF METHYL AND ETHYL CYANIDES[1]

BY B. S. RABINOVITCH[2] AND C. A. WINKLER[3]

Abstract

The products of pyrolysis of methyl and ethyl cyanides at 865° and 675° C. respectively have been determined at each of two flow rates. From methyl cyanide were obtained hydrogen, methane, hydrogen cyanide, and carbon. Small amounts of "C_2" hydrocarbons and high boiling materials were also formed. The results indicate that hydrogen cyanide is a primary product.

Ethyl cyanide yielded hydrogen, methane, ethane, ethylene, hydrogen cyanide, methyl cyanide, acrylonitrile, and carbon, together with small amounts of succinonitrile and higher boiling materials. The reaction is obviously complicated by secondary changes.

A kinetic study of the thermal decomposition of the lower aliphatic nitriles has been contemplated as part of a series of investigations into nitrile reactions. Although the catalytic cracking of higher fatty acid nitriles has been the subject of industrial research (5), no information about the thermal decomposition of the short chain members is reported. Therefore, before attempting a kinetic investigation, the pyrolysis of methyl and ethyl cyanides has been studied at different flow rates to obtain information about the nature of the reactions involved and the products formed.

Materials and Procedure

The nitriles were obtained commercially and purified by distillation. The materials used boiled over a range of 0.2° C.

Pyrolysis was effected in a silica tube, 55 cm. in length and 2 cm. in diameter, wound with a heating element and suitably insulated. Temperature was controlled manually and measured with a chromel-alumel thermocouple inserted at one end. Temperature variation along the tube was 10° C. Approximately 45 gm. of nitrile was injected into the furnace by mercury displacement from a burette. The tube was connected through graded seals to a series of traps maintained at temperatures of 100°, 0°, −78°, and −183° C. Liquid products were collected at 0° and 100° C., and gases condensed in the colder traps, or if not condensed, were bled off into evacuated flasks. A

---

[1] *Manuscript received January 27, 1942.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Postgraduate student, McGill University, and holder of a studentship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry, McGill University.*

constant operating pressure was thus maintained during an experiment. Experiments were made at two flow rates with each cyanide.

Gaseous products were analysed in a low-temperature still of the Podbelniak type, and liquid products were determined by distillation on a Whitmore column. In most instances, the identity of the products was verified by confirmatory tests.

Results

The results are shown in Table I.

TABLE I

PYROLYSIS AND ANALYTICAL DATA

Pyrolysis data	Ethyl cyanide at 675° C.		Methyl cyanide at 865° C.	
Flow rate, cc. liq./min.	1.0	0.22	0.80	0.23
Operating press., cm. Hg.	60	45	52	35
Percentage decomposed	64.5	98.5	48.4	94.6
Products	Moles/mole cyanide decomposed		Moles/mole cyanide decomposed	
H_2	0.24	0.32	0.24	0.99
CH_4	0.15	0.43	0.39	0.23
C_2H_4	0.18	0.032		
$C_2H_2 + C_2H_4$			0.043	0.012
C_2H_6	0.14	0.13		
HCN	0.42	0.79	0.85	0.86
CH_3CN	0.27	0.084		
$CH_2{=}CHCN$	0.24	0.10		
$(CH_2CN)_2$	0.024	0.024		
Higher boiling products	0.9*	0.7*	0.8*	0.4*
Carbon	1.8*†	5.8*†	3.4*†	6.2*†
Tar			0.7*	0.3*

* *Recorded in grams.*

† *A deposit of carbon was formed over the walls of the connecting tubing, and its estimation was difficult.*

The gaseous products from the methyl cyanide decomposition are hydrogen, methane, and small amounts of "C_2" unsaturated hydrocarbons. Their identities were confirmed by the usual combustion and absorption methods. Cyanogen was not found, either by distillation, or by methods outlined by Dennis (1).

In the liquid products from methyl cyanide, hydrogen cyanide (b.p. 26° C.) was identified by a boiling point of 25 to 27° C., and by formation of a white precipitate with silver nitrate. The small amount of higher boiling material was a light yellow liquid with the odour of benzonitrile. The liquid thickened and turned reddish-brown on standing.

The identities of the gaseous products from the ethyl cyanide decomposition —hydrogen, methane, ethylene, and ethane—were confirmed, again by combustion or absorption after the distillation.

The liquid products obtained from ethyl cyanide were separated into three fractions. One of these was identified as hydrogen cyanide from its boiling point and by silver nitrate precipitation. A second fraction had a boiling range from 75 to 84° C. Possible products boiling in this range are benzene (b.p. 80° C.), methyl cyanide (b.p. 81 to 82° C.), acrylonitrile (b.p. 78 to 79° C.) and ethyl isocyanide (b.p. 80° C.). The characteristic odour of ethyl isocyanide was absent, and the oxalic acid test and the hydrolysis analysis method of Guillemard (3) did not indicate its presence. Bromine was rapidly absorbed by the liquid mixture, however, and a bromide was prepared according to the method of Moureu (4) for acrylonitrile. Its boiling point was 125 to 132° C. at 58 mm., and its density 2.13 at 25° C. These identify it as the dibromide of acrylonitrile, with b.p. 126 to 129° C. at 55 mm. and density 2.16 at 0° C. The nitrilic character of the remaining portion of the fraction (methyl cyanide) was verified by hydrolysis, with production of an equivalent of ammonia.

The third fraction of the ethyl cyanide liquid products had a boiling range of 105 to 200° C. at 20 mm. Fractional distillation yielded a white solid of m.p. 50 to 51° C., which is in agreement with the melting point of 54.5° C. for succinonitrile; the boiling point of succinonitrile is 159° C. at 20 mm., which falls within the range of the third fraction. The remainder of the fraction was liquid at room temperature and probably contained other dinitriles. These might be $CH_2(CN)_2$, $(CH_2)_3(CN)_2$ and $(CH_2)_4(CN)_2$, which are liquids around room temperature and boil at temperatures throughout the range found. Traces of benzonitrile were also indicated by the characteristic odour.

Discussion

The thermal decomposition of methyl cyanide appears to proceed in a relatively simple manner. Hydrogen cyanide occurs in amounts substantially equivalent to methyl cyanide disappearance and apparently is a primary product. Hydrogen is produced to some extent at least by secondary reaction. The increases (with time) in the proportion of hydrogen and of "C_2" hydrocarbons can both be attributed to the decomposition of methane (6). Carbon is formed in large amounts, probably as a result of hydrocarbon decomposition and other cracking reactions at the high temperature employed.

The decomposition of ethyl cyanide is evidently very complex. Formation of hydrogen, methane, hydrogen cyanide, and carbon is partially due to secondary reactions; increase in their relative proportions with time is presumably due to partial decomposition of ethylene (6) and nitrilic products. Decomposition at 675° C. of the methyl cyanide formed possibly occurs as a result of sensitization by free radicals. Dehydrogenation of ethyl cyanide would account for the formation of acrylonitrile; the catalytic dehydrogenation of ethyl cyanide has been reported (2).

The ethyl cyanide decomposition does not appear suitable for kinetic study even at the lowest temperature (590° C.) at which decomposition is conveniently measurable. A kinetic study of the thermal decomposition of methyl cyanide in a temperature region around 800° C. is in progress.

References

1. Dennis, L. M. and Nichols, M. L. Gas analysis. Rev. ed. Macmillan Company, New York. 1929.
2. Farbenind., I.G. A.G. Fr. 790262, Nov. 16, 1935.
3. Guillemard, H. Ann. chim. phys. (Ser. 8) 14 : 311-432. 1908.
4. Moureu, M. C. Ann. chim. phys. (Ser. 7) 2 : 145-212. 1894.
5. Ralston, A. W., Harwood, H. J., and Pool, W. O. J. Am. Chem. Soc. 59 : 986-992. 1937.
6. Steacie, E. W. R. Chem. Rev. 22 : 311-402. 1938.

THE HYDROLYSIS OF ACID AMIDES IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS[1]

By B. S. Rabinovitch[2] and C. A. Winkler[3]

Abstract

The Arrhenius constants have been evaluated for the hydrolysis of formamide, acetamide, propionamide, and benzamide in hydrochloric acid solutions over the concentration range 1 to 10 *N*. There is approximate correspondence between reaction rates and activation energies for the series of amides. An increase in observed activation energy with increasing acid concentration was found for all amides. The maximum in rate of hydrolysis, which occurs at higher acid concentrations, is discussed and accounted for by the variation in the Arrhenius constants with acid concentration.

Introduction

The relations between reaction rate in solutions of electrolytes and such factors as concentration of electrolyte, mean ion activity, and the primary salt effect, have frequently been examined and discussed without regard to possible changes in the parameters A and E of the Arrhenius equation over the range of concentrations considered. While this may often be valid for dilute solutions, particularly for reactions of zero ionic type (2, 18), recent work on ionic reactions in dilute solution has shown the dependence of A and E on ionic strength and dielectric constant (27, 40). Similarly, the salt effect in such reactions has been shown to be related to changes in the Arrhenius constants (28, 29).

Little study has been made of the parameters of the Arrhenius equation for concentrated solutions of electrolytes. Here, the situation is more complicated. The consideration of the dependence of reaction rate on acid concentration necessarily involves the simultaneous variation of dielectric constant and composition of the medium. Other factors in addition to those present in dilute solution may also operate. v. Kiss and co-workers (22), in studies of the neutral salt effect in ionic reactions at high salt concentrations, have found that changes in the Arrhenius constants with salt concentration may occur. Leininger and Kilpatrick have recently found a change in the observed activation energy with change of acid concentration for hydrolysis of sucrose (25) and ethylal (26) in concentrated acid solutions, a behaviour they believe general for reactions in concentrated solutions of electrolytes. Where variation of the Arrhenius constants does occur, their determination over the range of acid concentration under consideration is obviously important, since in the absence of this information undue emphasis may be placed on less relevant factors in the interpretation of the rate of reaction.

[1] *Manuscript received January 27, 1942.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Holder of a Studentship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry, McGill University.*

Of the many reactions that might have been studied to obtain additional information on the changes in A and E with acid concentration, the hydrolysis of amides and nitriles in concentrated acids appeared of particular interest. Both reactions are of the zero ionic type, of which many studies have been made at a single temperature in dilute and concentrated acid solutions. Some determinations of activation energy for amide and nitrile hydrolysis have been made, but these usually refer to dilute solutions and appear in some instances to be rather unreliable. A fact of more interest, however, is that the effect of acid concentration on rate of hydrolysis is quite different for the two reactions. With amides, the unimolecular velocity constants increase slowly with acid concentration and pass through a maximum value at various acid concentrations from 3 to 6 N (23), depending on the amide concerned. The rate of nitrile hydrolysis, on the other hand, apparently increases continuously and more rapidly with acid concentration than any other reaction studied over a similar concentration range (24).

The purpose of the present paper is to present the results of an investigation on the hydrolysis of formamide, acetamide, propionamide, and benzamide in concentrated hydrochloric acid. The results for nitriles will be presented in a later paper.

Materials and Procedure

Formamide was obtained commercially and purified by repeated distillation *in vacuo*. Though traces of ammonium formate and water persist after such treatment (39), these should have no appreciable effect on the rate of hydrolysis. Solutions were stored at 0° C. after standardization and determination of the free ammonia content.

Acetamide, propionamide, and benzamide were also obtained commercially and purified by recrystallization. Their solutions were prepared directly by weight. The amide normalities in the various reaction mixtures were as follows:

Acid normality	1.00	4.00	6.48	8.47	10.13
Formamide	0.3971	0.3929		0.3940	
Acetamide	0.2039	0.2045		0.2032	
Propionamide	0.2025	0.2031	0.2033	0.1982	0.1991
Benzamide	0.0996	0.0998		0.04987	

Reagent grade hydrochloric acid was standardized by density determinations and by titration, and diluted to the required concentrations.

For experiments near room temperature, reaction solutions were prepared by mixing appropriate volumes of amide and acid solutions at 0° C. in stoppered, Pyrex reaction vessels. At higher temperatures, reaction took place in sealed Pyrex bulbs. In both cases, dead space was negligible. The reaction vessels were immediately immersed in thermostats regulated to within 0.1° C., temperatures being determined with standard thermometers. A correction, found experimentally, was made for the time required for solutions to reach the reaction temperature. For experiments below room temperature, the reactants were brought to the desired temperature before being mixed in the reaction vessel. Concentrations after mixing were calculated from density–composition data for hydrochloric acid (International Critical Tables). For this purpose, the dilute amide solutions were treated as pure water. Since the hydrolysis of amides yields ammonia and the corresponding acid, the course of the reaction, except with formamide, was followed by analysis for ammonia by Folin's aspiration method (15), calibrated and used at 0° C. A small correction, evaluated experimentally, was applied for the hydrolysis of unconverted amide during analysis. With formamide, this method caused decomposition of the unconverted amide and it was therefore replaced by the formol titration method for ammonia (19, p. 525).

Results

The unimolecular velocity constants obtained at different acid concentrations and temperatures for the four amides used are given in Table I. Each constant is the mean of five or six individual values that usually deviated from the recorded value by not more than 3%. No correction has been applied for concentration taken as at 25° C., nor for variation of collision number with temperature. These errors partially cancel each other, and should have negligible influence for comparison of activation energies at different acid concentrations. Comparison of the rate data with those available in the literature is difficult, extrapolation or interpolation usually being necessary. The general agreement is within experimental error. For comparative purposes within the present study, any systematic errors in rate determinations should largely cancel.

The values of A and E at different acid concentrations, for each amide, have been calculated from the Arrhenius relation: $k = A\epsilon^{-E/RT}$. The equation appeared to be satisfactorily obeyed in all cases. In evaluating a bimolecular value of log A, which is included for purposes of illustration in later discussion, the velocity constants, expressed in seconds, were divided by acid normality. The results of these calculations are given in Table II, together with values obtained directly or calculated from the data of other workers. In a number of these investigations, the erroneous procedure has been followed of expressing the results as a temperature coefficient, which is obviously temperature dependent, and using the value so obtained for discussion and for comparison with data obtained at different temperatures.

It is evident from Table II that the activation energies increase with acid concentration. The changes with formamide and benzamide are only about 1000 cal. for the whole concentration range, but consideration of the plots of log k against temperature shows that the relative values are less than 500 cal. in error. The fact that the changes for these two amides are in the

TABLE I

VELOCITY CONSTANTS FOR THE HYDROLYSIS OF AMIDES WITH HYDROCHLORIC ACID

Temp., °C.	$k \times 10^3$ hr.$^{-1}$				
	Concentration of acid, normality				
	1.00*	4.00	6.48	8.47	10.13
Formamide					
0.0	2.84	10.7		5.30	
14.8		60.3			
19.8	28.5	99.4		57.5	
24.7	49.2	178.		102.	
29.4	77.1			161.	
Acetamide					
40.6	13.2	16.9		4.02	
45.7	20.6	29.4			
51.9		50.6			
52.0				12.8	
59.6	71.4	107.		26.9	
70.7	183.			80.0	
Propionamide					
29.0		9.01			
29.5	5.78		4.62		
40.5	16.4	29.4	13.2	5.88	3.17
49.9		74.7			
50.1	39.6		36.0	17.0	8.87
59.6	95.8	170.	83.8	41.9	22.6
69.6				95.5	
70.8					66.6
Benzamide					
48.7		3.55		1.73	
59.6	3.44	11.0		5.58	
68.7	8.59	27.0		13.9	
78.6	18.7	63.8		34.3	
89.6	52.9				

* *At this concentration, a downward drift in velocity constants, due to depletion of the catalyst by ammonia formation, occurs; the bimolecular constants are satisfactory.*

same direction as the larger increases observed for acetamide and propionamide also indicates that the observed E changes are significant.

The variation of the values of log A with acid concentration appears to be similar for all amides. For a given amide, the unimolecular log A values increase with increase in E, as is commonly observed. The bimolecular values (Column 3, Table II) increase from 1 to 4 N and then tend to remain constant or decrease at higher acid concentrations. However, since the total variation of log A is small, and since it is uncertain whether normality is the proper function of acid concentration by which k should be divided, stress is not placed on this behaviour.

TABLE II

ARRHENIUS CONSTANTS FOR EACH AMIDE AT VARIOUS HYDROCHLORIC ACID CONCENTRATIONS

Amide	Acid concentration, normality	Log A		E, cal.		Remarks
		Based on k/N	Based on k	This investigation	Previous investigations	
Formamide	1.00	9.6	9.6	18,400	19,100[1]	[1] Crocker (9). A systematic difference exists between the present results and those of Crocker, which are invariably higher. Kilpi (21) has noted some discrepancies between his velocity constants and those of Crocker. It may be that some systematic error has entered into the latter's results, which otherwise appear to be of good precision.
	4.00	9.7	10.3	18,500		
	8.47	9.7	10.6	19,300		
Acetamide	1.00	8.7	8.7	18,800	20,780[1]	
					15,900[2]*	
					18,800[3]	
					15,500[4]*	
	4.00	9.0	9.6	20,000	20,600[5]*	
	5.00				21,000[5]*	
	8.47	8.9	9.8	21,200		
Propionamide	1.00	8.6	8.6	18,600	19,830[1]	[2] Euler and Rudberg (14). The average error in the velocity constants used was as high as 15%. Acid concentration was approximately 0.1 N.
					14,400[4]*	
	4.00	8.8	9.4	19,400		
	6.48	8.5	9.3	19,700		
	8.47	8.4	9.3	20,200		
	10.13	8.8	9.8	21,300		
Benzamide	1.00	9.2	9.2	21,700		[3] Moelwyn-Hughes (32, p. 245). Calculated from the results of several workers at about 1 N acid.
	4.00	9.3	9.9	21,900		
	8.47	9.1	10.0	22,600		
						[4] v. Peskoff and Meyer (34)
						[5] Taylor (38)

* *Based on two temperatures only.*

Discussion

The acid catalyzed hydrolysis of amides has usually been interpreted on the basis of Euler's theory of interacting ions (11, 12, 13). While the theory is useful for discussion of certain reactions, there have been serious objections to its general validity (6). As applied to the acid catalyzed hydrolysis of amides, where amide cation is considered the reacting species, the equilibrium formation of the cation may instead be considered as a preliminary step in the formation of an activated intermediate. This viewpoint renders unnecessary the improbable assumptions of Euler concerning the activation of the cation.

The maximum in the rate of hydrolysis, as given by the unimolecular velocity constants, was first observed for acetamide (5) and has been shown to be general for the acid catalyzed hydrolysis of amides (23). This maximum has usually been interpreted as being due to the occurrence of a maximum concentration of an amide cation at a certain acid concentration (5, 13, 23, 36). With different amides and a given acid, or with different acids and a given amide, the acid concentration at the maximum might be expected to have different values, and this is, in fact, the observed behaviour.

There is considerable disagreement concerning the structure of the cation. However, the imide structure seems to be favoured in some recent kinetic work (23, 35). Some of the data from dipole moments and absorption spectra measurements indicate that amides exist mainly in the imide form in aqueous solution (3). The fact that disubstituted amides, CH_3CONR_2, for which the imide structure is not possible, are hydrolyzed very slowly, as indicated by qualitative examination (1, 31), would also seem to suggest that the reactive cation is of the imide form.

The decrease in hydrolysis rate following attainment of the maximum has been variously explained. It has been suggested that at higher acid concentrations an unreactive, undissociated salt is formed (5, 13). In opposition to this, it has been pointed out that the acid concentration corresponding to the maximum should depend on amide concentration, and it is stated that this is not in agreement with experiment (23). This criterion of undissociated salt formation does not take into account possible complications arising from change in degree of dissociation of the amide with change of amide concentration. More data would seem necessary to check these points. It should be borne in mind, moreover, that high amide concentrations might introduce changes arising simply from changes in reaction conditions as non-electrolyte concentration is altered.

The decrease in rate after the maximum has been ascribed by Krieble and Holst (23) to direct proportionality between rate and square of the activity of water, after a maximum constant concentration of cation is reached. However, existing data indicate that the rate constants, at the same acid concentrations, fall off more markedly with acetamide and propionamide than with formamide and, possibly, benzamide, whereas the proportional decrease would be expected to be the same for all amides if decrease in activity of water alone determined the decrease in rate constant. As these authors have pointed out, however, the available rate data at high acid concentrations are scanty and more measurements would be desirable. Alternatively, it has been suggested by the same authors that increased acid concentration might favour the original amide and thus lower the concentration of cation. Relevant to this suggestion, measurements of the base dissociation constants of amides over the range of acid concentrations concerned would be of interest.

The changes in reaction rates with acid concentration may be accounted for by the observed changes in A and E (Table II). In terms of the unimolecular constants, the rates pass through a maximum in the region of acid concentrations of 3 to 6 N, while on the basis of the bimolecular constants they show steady decrease with increasing acid concentrations. If the reaction proceeds by way of an equilibrium cation, the unimolecular constants should reach, but not pass through, a maximum. This behaviour corresponds to a dominant effect of E change, since, while E increases for all the amides, the A values, corresponding to unimolecular or bimolecular constants, either increase more slowly than E or pass through a maximum at higher acid concentration.

The influence of the nature of the amide on the rate of hydrolysis is indicated in Fig. 1. Obviously there is approximate correspondence between rate and activation energy, at each of the several acid concentrations. Defect from exact linearity can be attributed to simultaneous variations in energy and entropy of activation. This behaviour is commonly observed for aliphatic compounds, where, as in the present instance, the substituent is close to the reacting group (20, 41). It would be interesting to study meta- and para-substituted amides, since with these derivatives only minor variations in entropy of activation occur (16, pp. 121, 208, 244).

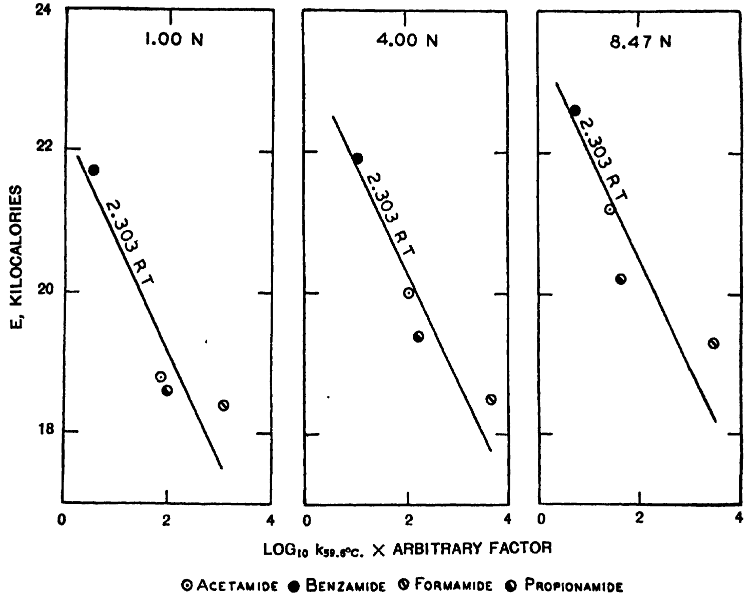


FIG. 1. *Plot of log k against E for different amides at three acid concentrations.*

Proportionality between the rate constants for different amides and the dissociation constant of the corresponding carboxylic acids has been suggested by Crocker (9) for the acid catalyzed hydrolysis, and by Calvet (7) for the alkaline hydrolysis of amides. Hammett (16, pp. 121, 208, 244) has pointed out, however, that in general, linear free energy relations do not apply to reactions of aliphatic compounds where variation of structure from member to member of a series causes variation in entropy of activation. For the acid hydrolysis of aliphatic amides, there is not even qualitative dependence of rate constants on dissociation constants of the acids. For example, the rate of hydrolysis of propionamide is greater than that of acetamide, although the dissociation constant of propionic acid is smaller than that of acetic acid. The relations are also inverted for benzamide relative to acetamide or propionamide.

The magnitude of the *A* factor (Table II) places the acid catalyzed hydrolysis of amides in the category of "slow" reactions, as previously pointed out by Christiansen (8). Reactions involving ions generally have "normal" rates in aqueous solution (33). The relative slowness of amide hydrolysis might be due to the fact that if the reacting species is the amide cation, the concentration of which is appreciably lower than the amide concentration in dilute solution (13), the calculated velocity constants will be lower than the true values. The cation concentration increases with acid concentration, however, and it might be expected that at high acid concentrations the rate would become more nearly normal. The observed *A* values do actually increase with acid concentration (Table II, Column 4). However, since *E* increases, and parallel variation of *A* and *E* is commonly observed, the increase in *A* cannot here constitute a criterion of the validity of this explanation.

It is interesting to note that if the reaction is treated on the basis of ternary collisions, normal *A* values result (33) and the magnitude and direction of changes in *E* with acid concentration may be altered. However, viscosity data for hydrochloric acid solutions are not extensive and this treatment has not been applied to the present data.

The change in the Arrhenius activation energy with change of acid concentration is specific for different amides (Table II). It might be that a small temperature dependence of *A* and *E* would suffice to make the observed *E* values deviate from the true (4). Moreover, if the temperature dependence of *E* varies with concentration of acid, the deviation from the true value will similarly vary, and the observed values will apparently vary with concentration. Hydrolysis reactions are of a type that are known to exhibit temperature dependence of *E* (30). Moreover, there are indications that such an effect exists in the alkaline hydrolysis of amides (10, 30). It is not possible, from the data of this investigation, to exclude temperature dependence of the Arrhenius constants. Very accurate measurements are necessary to determine the magnitude of the temperature coefficient of *E*, since it is often very small. However, no indication of an *E* change with temperature has been given by the work of Crocker (9), the precision of which appears to be of the requisite order. Furthermore, the variations in *A* and *E*, if they do occur, usually tend to cancel each other. The correspondence between change of rate and change of *E* also indicates that the *E* change is fundamental.

It is probable that changes in *E* depend simply upon variation of reaction conditions, but it might be that there is a change in mechanism as acid concentration is altered. Euler and Ölander (13) have indicated that complexity may attach to the mechanism for the hydrolysis of acetamide at higher acid concentrations. It may be noted that hydrolysis of amides does not give the theoretical relation between rate constant and acidity function of Hammett required for specific hydrogen ion catalysis (23). This is of particular interest, since Euler's theory, does, in part, form the basis of Hammett's treatment (17).

This might indicate that mechanisms other than that involving the equilibrium formation of an amide cation may occur. However, the failure is not conclusive, since Hammett's assumptions might not be fulfilled here (42). The work of Reitz (36) on the heavy water hydrolysis indicates specific hydrogen ion catalysis, although objection to the Bonhoeffer-Reitz criterion has been raised (37).

References

1. ALBERTI, C. Gazz. chim. ital. 69 : 150-162. 1939.
2. AMIS, E. S. and HOLMES, F. C. J. Am. Chem. Soc. 63(8) : 2231-2235. 1941.
3. AUWERS, K. v. Ber. 70B(5) : 964-967. 1937.
4. BELL, R. P. Trans. Faraday Soc. 34 : 229-236. 1938.
5. BENRATH, A. Z. anorg. allgem. Chem. 151 (1 and 2) : 53-67. 1926.
6. BRÖNSTED, J. N. Chem. Rev. 5(3) : 231-338. 1928.
7. CALVET, E. J. chim. phys. 30 : 198-212. 1933.
8. CHRISTIANSEN, J. A. Z. physik. Chem. 113(1 and 2) : 35-52. 1924.
9. CROCKER, J. C. J. Chem. Soc. 91 : 593-612. 1907.
10. CROCKER, J. C. and LOWE, F. H. J. Chem. Soc. 91 : 952-962. 1907.
11. EULER, H. v. Z. physik. Chem. 32(2) : 348-359. 1900.
12. EULER, H. v. Z. physik. Chem. 36 (6) : 641-663. 1901.
13. EULER, H. v. and ÖLANDER, A. Z. physik. Chem. 131 (1 and 2) : 107-126. 1928.
14. EULER, H. v. and RUDBERG, E. Z. anorg. allgem. Chem. 127(3) : 244-256. 1923.
15. FOLIN, O. and FARMER, C. J. J. Biol. Chem. 11(5) : 493-501. 1912.
16. HAMMETT, L. P. Physical organic chemistry. McGraw-Hill Book Company, Inc., New York and London. 1940.
17. HAMMETT, L. P. and PAUL, M. A. J. Am. Chem. Soc. 56(4) : 830-832. 1934.
18. HARNED, H. S. and ROSS, A. M., JR. J. Am. Chem. Soc. 63(7) : 1993-1999. 1941.
19. HAWK, P. B. Practical physiological chemistry. 7th ed. P. Blakiston's Son and Company, Philadelphia. 1920.
20. HINSHELWOOD, C. N. and LEGARD, A. R. J. Chem. Soc. 587-596. 1935.
21. KILPI, S. Z. physik. Chem. 80(2) : 165-191. 1912.
22. KISS, A. and BOSSANYI, I. Rec. trav. chim. 53 : 903-916. 1934.
23. KRIEBLE, V. K. and HOLST, K. A. J. Am. Chem. Soc. 60(12) : 2976-2980. 1938.
24. KRIEBLE, V. K. and NOLL, C. I. J. Am. Chem. Soc. 61(3) : 560-563. 1939.
25. LEININGER, P. M. and KILPATRICK, M. J. Am. Chem. Soc. 60(12) : 2891-2899. 1938.
26. LEININGER, P. M. and KILPATRICK, M. J. Am. Chem. Soc. 61(9) : 2510-2514. 1939.
27. LA MER, V. K. and co-workers. J. Am. Chem Soc. 1933 *et seq.*
28. LA MER, V. K. and KAMNER, M. E. J. Am. Chem. Soc. 57(12) : 2662-2668. 1935.
29. LA MER, V. K. and KAMNER, M. E. J. Am. Chem. Soc. 57(12) : 2669-2673. 1935.
30. LA MER, V. K. and MILLER, M. L. J. Am. Chem. Soc. 57(12) : 2674-2680. 1935.
31. MAXIM, N. and ZUGRAVESCU, I. Bull soc. chim. (Sér. 5) 1 : 1087-1099. 1934.
32. MOELWYN-HUGHES, E. A. Kinetics of reactions in solution. Oxford University Press, London. 1933.
33. MOELWYN-HUGHES, E. A. Acta Physicochim. U.R.S.S. 4(2) : 173-224. 1936.
34. PESKOFF, N. v. and MEYER, J. Z. physik. Chem. 82(2) : 129-171. 1913.
35. RAMART-LUCAS, P., NAIK, K. G., and TRIVEDI, R. K. Bull. soc. chim. (Sér. 5) 1 : 525-538. 1934.
36. REITZ, O. Z. physik. Chem. A, 183(5) : 371-391. 1939.
37. ROBERTS, I. and UREY, H. C. J. Am. Chem. Soc. 61(10) : 2584-2587. 1939.
38. TAYLOR, T. W. J. J. Chem. Soc. : 2741-2750. 1930.
39. VERHOEK, F. H. J. Am. Chem. Soc. 58(12) : 2577-2584. 1936.
40. WARNER, J. C. Ann. New York Acad. Sci. 39(5) : 345-354. 1940.
41. WATSON, H. B. *et al.* Ann. Rept. Chem. Soc. (London) 35 : 204-251. 1938.
42. WYNNE-JONES, W. F. K. Trans. Faraday Soc. 34 : 245-251. 1938.

PASTURE STUDIES

XXIII. A PROPOSED MODIFICATION OF THE FLUORIMETRIC METHOD FOR THE ESTIMATION OF RIBOFLAVIN[1]

By R. A. Chapman[2] and W. D. McFarlane[3]

Abstract

The fluorimetric method for the determination of riboflavin in foodstuffs has been modified to permit the use of the fluorimeter described by Froman and McFarlane (4). Extracts are prepared by enzymatic digestion and purified by barium chloride precipitation and benzyl alcohol extraction. Photochemical reduction of riboflavin in the 'blank' is effected by stannous chloride in benzyl alcohol solution.

Introduction

Numerous methods, based on the measurement of the intensity of the yellow-green fluorescent light emitted when the solution is irradiated with light of certain wave-lengths, have been proposed for the determination of riboflavin. The riboflavin has generally been extracted from tissues by means of acetone or methanol and the extract purified by adsorption on Franconite, Floridin earth or lead sulphide, etc. Adsorption effects only a partial removal of substances that interfere with the fluorimetric reading, and further purification is necessary. Emmerie (2) and Conner and Straub (1) employed controlled oxidation with permanganate and hydrogen peroxide. Sullivan and Norris (9) used sodium hydrosulphite and estimated the riboflavin from the difference between the fluorescence readings of the reduced and unreduced samples. Benzyl alcohol was used by Emmerie (3) to separate riboflavin from interfering substances in the extract, Greene and Black (5) having shown it to be the best solvent.

After a careful study of these various methods the writers have developed a simple and rapid modified procedure that omits the adsorption step and employs *(a)* benzyl alcohol as an immiscible solvent for the extraction of riboflavin, *(b)* barium chloride solution for the removal of impurities in the extract, and *(c)* a benzyl alcohol solution of stannous chloride for the preparation of the blank. Since this investigation was completed, Najjar (8) has proposed a procedure using a pyridine–butyl-alcohol mixture as the immiscible solvent. However, the writers have found benzyl alcohol to be quite satisfactory and its use has certain advantages in the particular procedure reported herein.

Experimental

Acid extraction (1) or extraction with an acid–acetone mixture (9) have been the chief methods proposed for the preparation of a crude extract from tissues. Benzyl alcohol is miscible with acetone, and phosphoric esters of

---

[1] *Manuscript received in original form December 31, 1941, and as revised, March 14, 1942.*
Contribution from the Macdonald College Pasture Committee, Faculty of Agriculture (McGill University), Macdonald College, Que. Macdonald College Journal Series No. 170.

[2] *Research Assistant, Macdonald College Pasture Committee.*

[3] *Professor of Chemistry.*

riboflavin are not extracted by benzyl alcohol. Therefore it appeared logical to use pepsin and takadiastase digestion as in the determination of thiamine (7) so that simultaneous estimation of riboflavin and thiamine would also be possible. Pepsin extraction, compared with acid extraction, gave slightly higher and more reproducible results; this confirmed Van Duyne's (10) findings. Incubation at 37° C. must be carried out in a dark cabinet, but no special precautions need be taken to exclude light at any other stage in the determination.

Benzyl alcohol alone formed, with various extracts, heavy emulsions that were very difficult to break. A further disadvantage lay in the fact that the benzyl alcohol, having the greater density, separated as the lower layer along with a certain amount of precipitated material, thus making it necessary to use suction and filtration. These difficulties were overcome by adding a barium chloride solution, which reduced the tendency for emulsions to form, precipitated impurities in the extract, and increased the density of the aqueous phase so that the clear benzyl alcohol extract remained on the top. Zinc acetate is a better precipitant than barium chloride, but it is appreciably soluble in benzyl alcohol and forms a cloudy precipitate with stannous chloride.

For the preparation of the blank, a benzyl alcohol solution of stannous chloride was found to be the best of a number of reducing agents tried. The reduction of riboflavin to the non-fluorescent state by stannous chloride took place rapidly only under the influence of ultra-violet radiations. This observation supports the contention of Haring and Walton (6) that the autoxidation of stannous chloride is a photochemical chain reaction. It was found necessary to twice recrystallize the stannous chloride from hot 95% ethanol to remove impurities that cause turbidity. In the analysis of many materials, pure benzyl alcohol gave exactly the same instrument reading as a blank prepared by reduction with stannous chloride. However, some extracts contained substances other than riboflavin that were extracted by benzyl alcohol and exhibited a yellowish fluorescence in ultra-violet light that was not abolished by stannous chloride. In such cases a significant error was introduced when pure benzyl alcohol was used as the blank, and therefore a blank prepared by treating an aliquot of the test solution with stannous chloride must be employed.

The fluorescence measurements were made with the instrument described by Froman and McFarlane (4), employing a Corning red-purple Corex No. 986 filter between the ultra-violet lamp and the solution. A Corning No. 511 filter gave a smaller reading with the blank and a greater galvanometer deflection for the same concentration of riboflavin, but the reduction of riboflavin by stannous chloride in blue light is much slower than in ultra-violet light.

PROCEDURE

Transfer a 5 to 20 gm. sample, the weight depending on the vitamin content, to a 250 ml. centrifuge bottle and add 50 to 75 ml. of a 0.2% pepsin solution in 0.33% hydrochloric acid. Let stand for one hour in the dark and adjust to pH 2.0 with *N* hydrochloric acid or *N* sodium hydroxide, using thymol blue as an external indicator. Incubate overnight at 37° C. (excluding light), adjust to pH 4.5, using bromcresol green as an external indicator, add 0.1 gm. of takadiastase and incubate in the dark at 37° C. for a further three to four hours. Centrifuge at maximum speed, transfer the supernatant to a 100 ml. volumetric flask; wash the residue twice with distilled water, combine the extract and washings, and dilute to volume with distilled water. Store the extract in the dark until ready to complete the analyses as follows.

Pipette 3 ml. of the extract into each of two 15 ml. graduated centrifuge tubes, and to each add 2 ml. of a saturated aqueous solution of barium chloride and 7 ml. of benzyl alcohol. Shake thoroughly, but not too vigorously, for about one minute and centrifuge at maximum speed for about 10 minutes until the upper benzyl alcohol layer is quite clear. Note the volume of the benzyl alcohol layer and pipette 5 ml. of each into two fluorimeter tubes. To one tube add 0.5 ml. of 95% ethanol and 0.5 ml. of pure benzyl alcohol, and to the other (blank control) add 0.5 ml. of 95% ethanol and 0.5 ml. of a 3% solution of stannous chloride in pure benzyl alcohol.

Invert each tube several times to ensure complete mixing. Place the blank in the instrument (4) and expose to ultra-violet light for approximately three minutes until the galvanometer remains steady. Adjust the galvanometer to zero reading with the blank in position, substitute the test solution, and rotate the polaroids until the galvanometer again reads zero. Replace the

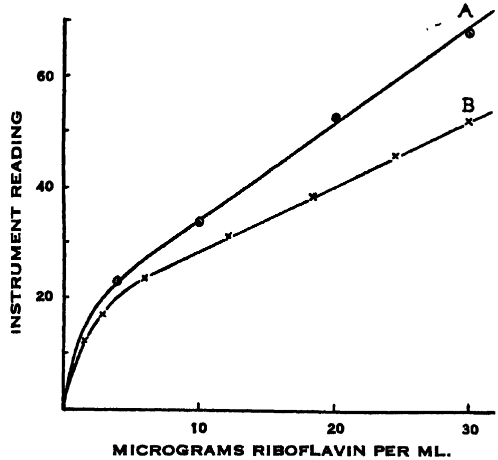


Fig. 1.—Calibration curves of riboflavin in (a) aqueous solution and (b) benzyl alcohol extract. (This graph also indicates the percentage extraction of riboflavin from aqueous solution by benzyl alcohol.)

test solution with the blank to ensure that the voltage has not changed appreciably. Convert the polaroid reading to micrograms of riboflavin by reference to a standard calibration curve (Fig. 1) prepared from data obtained with aqueous solutions of pure riboflavin treated in a manner identical with that of the actual test. Calculate the riboflavin content as follows:—

$$A \times 6 \times B/5 \times 100/3 \times 1/C = \text{micrograms per gm.}$$

where A = reference graph reading in micrograms per millilitre,
B = volume of the benzyl alcohol layer,
C = weight of original sample in grams,
6 = ml. of solution taken for test.

The data in Fig. 1 also indicate the percentage extraction of riboflavin from aqueous solutions by benzyl alcohol. The percentage extraction varies with the concentration, and hence the value of K in the equation

$$C = K \sin^2 \theta$$

is a variable quantity (4).

The writers have found that waste benzyl alcohol can be very satisfactorily reclaimed by the following procedure. Add a 20% solution of trichloracetic acid to give a 10% solution in benzyl alcohol. Shake, centrifuge, and siphon off the benzyl alcohol from the aqueous layer. Filter the benzyl alcohol and distill. The use of a fractionating column is unnecessary in the distillation.

Results

Recovery experiments were conducted on a number of products with the results shown in Table I. The readings obtained on different aliquots of

TABLE I

REPRODUCIBILITY OF THE READINGS OBTAINED WITH DIFFERENT ALIQUOTS OF THE SAME EXTRACT, AND RECOVERY OF RIBOFLAVIN ADDED TO DIFFERENT PRODUCTS

Material	Instrument reading	Micrograms per ml.	Riboflavin added, micrograms	Recovery of riboflavin, %
Liver meal	*(a)** 20.7 *(b)* 20.1 *(c)* 20.1	0.54 0.51 0.51	30.0	100.5
Skim-milk powder	*(a)* 12.5 *(b)* 12.4 *(c)* 12.5	0.14 0.14 0.14	25.0	97:3
Bread	*(a)* 11.3 *(b)* 11.9 *(c)* 12.0	0.12 0.13 0.13	21.8	97.6
Yeast	*(a)* 11.1 *(b)* 11.2 *(c)* 10.8	0.12 0.12 0.12	21.8	97.6
Whey powder	13.1	0.16	21.8	93.5

* *Aliquots of the same extract before riboflavin added.*

the same extract were quite constant and the recoveries of added riboflavin good. The sample of whey powder was badly caramelized, and the lower recovery may have been due to interference by pigments.

TABLE II

THE RIBOFLAVIN CONTENT OF VARIOUS MATERIALS AS DETERMINED BY THE MODIFIED METHOD

Material	Riboflavin, micrograms per gm.		Material	Riboflavin, micrograms per gm.	
	Author's method	Range of values given in the literature		Author's method	Range of values given in the literature
Calf liver	32.0	32.0 - 40.0	Chicken liver	18.6	—
Bran	2.7	3.17	Egg yolk	5.2	5.0 - 6.0
Whole wheat flour	1.7	0.89 - 2.03	Egg white	3.1	4.0 - 5.0
Buttermilk powder	31.3	—	Grass clippings	1.8	0.5 - 1.4
Dried yeast	18.7	18.0 - 21.0	Whole milk	1.0	1.0 - 3.0
Skim-milk powder	26.4	19.0 - 29.0	Whey powder	28.1	18.1 - 25.0

The possibility of destruction of riboflavin during enzymatic digestion was checked by carrying out the entire procedure with a pure riboflavin solution, and 98.5% of the riboflavin was recovered. The riboflavin content of a variety of materials as determined by the modified procedure is given in Table II. The simultaneous estimation of riboflavin and thiamine (7) has been carried out on aliquots of the same extract of various materials with satisfactory results.

Acknowledgment

One of the writers (R.A.C.) is a recipient of a grant from the Macdonald College Pasture Committee through Prof. L. C. Raymond.

References

1. Conner, R. T. and Straub, G. J. Ind. Eng. Chem. Anal. Ed. 13 : 385-388. 1941.
2. Emmerie, A. Nature, 138 : 164. 1936.
3. Emmerie, A. Rec. trav. chim. 58 : 290-292. 1939.
4. Froman, D. K. and McFarlane, W. D. Can. J. Research, B, 18 (8) : 240-245. 1940.
5. Greene, R. D. and Black, A. J. Am. Chem. Soc. 59(10) : 1820-1823. 1937.
6. Haring, R. C. and Walton, J. H. J. Phys. Chem. 37(3) : 375-380. 1933.
7. McFarlane, W. D. and Chapman, R. A. Can. J. Research, B, 19(5) : 136-142. 1941.
8. Najjar, V. A. J. Biol. Chem. 141(2) : 353-364. 1941.
9. Sullivan, R. A. and Norris, L. C. Ind. Eng. Chem. Anal. Ed. 11(10) : 535-540. 1939.
10. Van Duyne, F. O. J. Biol. Chem. 139(1) : 207-218. 1941.

THE ALKALOIDS OF *LYCOPODIUM* SPECIES

I. *LYCOPODIUM COMPLANATUM* L.[1]

By Richard H. F. Manske[2] and Léo Marion[2]

Abstract

Lycopodium complanatum L. has yielded a total of eight alkaloids, six of which appear to be new. They are complanatine (L1) ($C_{18}H_{31}ON$); alkaloid L2 ($C_{18}H_{29}O_2N$); alkaloid L3 ($C_{18}H_{31}O_2N$); alkaloid L4 ($C_{16}H_{27}N$); alkaloid L5 ($C_{18}H_{28}O_2N_2$); obscurine (L6) ($C_{18}H_{28}ON_2$); the known lycopodine ($C_{16}H_{25}ON$); and nicotine. It is pointed out that this is the first recorded occurrence of nicotine in a pteridophyte. The isolation of nicotine from *Equisetum arvense* L. is also recorded.

Vascular plants are divided into two great divisions, Pteridophyta and Spermatophyta. Chemists have devoted most of their energies to the chemical examination of plants belonging to the latter division, i.e., the flowering plants. The pteridophyta, sometimes called vascular cryptogams, are of secondary economic importance and frequently inconspicuous in appearance. They have received comparatively little attention from chemists. Certainly only a very few alkaloids from this source have been obtained in a pure state, and the constitution of none of these had until now been determined.

The family Lycopodiaceae includes the monotypic Australian genus *Phyloglossum* and the ubiquitous genus *Lycopodium* comprising some 180 species. The authors have examined five species native to the western extremes of the Lautentian Plateau and now report on the alkaloids isolated from *L. complanatum* L. The same plant was first examined in 1881 by Bödeker (2) who reported the occurrence of an alkaloid, lycopodine, to which he assigned the formula $C_{32}H_{52}O_3N_2$. Recently Achmatowicz and Uzieblo (1) gave the same name to one of three alkaloids that they isolated from *L. clavatum* L. They assigned the formula $C_{16}H_{25}ON$ to the base, which melted at 114 to 115° C. as recorded by Bödeker. It has now been shown that the chief alkaloids from these two plants of American origin are identical and presumably also identical with the lycopodine of previous authors. The same alkaloid has now been found in several other species. It yields analytical figures in best agreement with $C_{16}H_{25}ON$.

It has been possible to isolate a total of eight alkaloids from *L. complanatum*. In order to avoid cumbersome and perhaps inappropriate names, it has been deemed expedient to designate the individual alkaloids by a number following the capital L. Where the homogeneity and purity of the bases do not seem to be in doubt, a trivial name may also be given. Thus alkaloid L1, best represented by $C_{18}H_{31}ON$, has been termed complanatine. The empirical formula of L1 and those of L2 ($C_{18}H_{29}O_2N$), of L3 ($C_{18}H_{31}O_2N$), and of L4

---

[1] *Manuscript received February 12, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1052.

[2] *Chemist.*

($C_{16}H_{27}N$) make it probable that these alkaloids are closely related to lycopodine. On the other hand, two new alkaloids, containing two nitrogen atoms each, may ultimately prove to possess a radically different structure. One of these, L6 ($C_{18}H_{28}ON_2$), has been termed obscurine since it was first obtained from *L. obscurum*. The other, L5 ($C_{18}H_{28}O_2N_2$), is empirically closely related to obscurine but has been found only in *L. complanatum*. It may be pointed out that the above formulae are mostly based on analyses of the perchlorates. Exclusive of lycopodine and complanatine there was available less than 1 gm. of each of the bases. When more material becomes available, efforts to confirm the formulae will be made.

Lastly, the occurrence of nicotine in this plant is reported. The total amount present is of the order of parts per million of the dried plant. Some, but not all, of the other species have also yielded nicotine. Furthermore, the authors have found it in *Equisetum arvense* L., although the total yield of alkaloids from this plant is extremely small and no other bases could be obtained in a pure state. The occurrence of nicotine in a number of flowering plants is now a matter of common knowledge. Aside from its presence in *Nicotiana* and *Duboisia* species it has recently been found in *Asclepias syriaca* L. (3). The occurrence of the same alkaloid in distantly related plants is no longer considered astonishing. Nevertheless, nicotine is the only alkaloid that has bridged the gap between Pteridophyta and Spermatophyta, it being present in no fewer than four orders, namely, Equisetales, Lycopodiales, Gentianales, and Polemoniales.

The authors have also investigated, but only in a preliminary way, the nature of the water insoluble polysaccharides of the plant. Hydrolysis with boiling dilute sulphuric acid yielded an appreciable amount of galactose. A search for fucose, and mannose, sugars present in the polysaccharide of marine algae, proved negative.

Experimental

The material, which was collected in October, was air-dried, ground to suitable size, and extracted in Soxhlet apparatus with methanol. There was available 65 kg. The following procedure has been adopted as standard in the investigation of all *Lycopodium* species thus far examined. It is given in considerable detail because it is not intended to repeat it in later communications.

Procedure

The methanolic extract was largely freed of methanol, water was added, and the remainder of the solvent boiled off. Hydrochloric acid was added until the mixture was distinctly acid to Congo red. Hot water was added until the volume was approximately one litre for every three kilos of plant material. The thoroughly stirred mixture was allowed to cool slowly and to stand undisturbed for several days. At the end of this time it was possible to decant a reasonably clear aqueous solution from the semisolid mixture of fats and other water insoluble substances. (In the case of *L. lucidulum* the insoluble matter remained in suspension but it proved to be unusually easy to filter and wash.) The insoluble residues were heated again with very dilute hydrochloric acid, the mixture was allowed to cool, and the decantate added to the next lot. The aqueous extract was filtered through a layer of charcoal, basified with excess ammonia, and repeatedly extracted with chloroform. The solvent was removed from the extract and the residue heated with an excess of dilute hydrochloric acid. The cooled solution was filtered with the aid of charcoal and extracted with ether until nothing further was removed. The aqueous solution was then basified with ammonia, and the liberated bases were extracted with several portions of ether. (The bases from *L. lucidulum* are not completely soluble in ether, and the ether insoluble portion was subsequently extracted with chloroform.) The combined extract was washed with water, the solvent removed, and the residue dried *in vacuo*. This will be referred to as the 'crude alkaloid'.

Lycopodine

The crude alkaloid was slowly distilled *in vacuo*, the distillation flask being heated in an air bath. The following fractions were collected—

(I) 85 to 95° (2 mm.)
(II) 150 to 160° (3 mm.)
(III) 175 to 185° (2 mm.)
(IV) Residue.

Fraction (II) was dissolved in ether and inoculated with a crystal of lycopodine. The crystals were filtered off, washed with ether, and recrystallized first from dry ether and then from hexane. As thus obtained, lycopodine melts not quite sharply at 116°.* By working up the mother liquors by further crystallization and distillation it was possible to obtain a satisfactory amount of crystalline base, but until it was observed that most of the lycopodium alkaloids form crystallizable perchlorates complete separation was not accomplished. The perchlorate of lycopodine is sparingly soluble in methanol or water and virtually insoluble in acetone and other organic solvents. It crystallizes from hot water in brilliant prisms that melt with some decomposition at 283° C. but without appreciable previous charring or shrinking. Found: C, 77.73; H, 10.38; N, 6.00, 6.01%. Calc. for $C_{16}H_{25}ON$: C, 77.73; H, 10.12; N, 5.66%. The perchlorate crystallizes without solvent of crystallization. Found: C, 55.51, 55.66; H, 7.72, 7.65; N, 3.92, 4.13%. Calc. for $C_{16}H_{25}ON \cdot HClO_4$: C, 55.25; H, 7.48; N, 4.03%.

Complanatine (L1)

The combined mother liquor from the crystallization of the lycopodine was freed of solvent and the viscous residue dissolved in methanol-acetone. A 60% aqueous solution of perchloric acid was added, drop by drop, until the mixture was just acid to Congo red. The copious crop of lycopodine perchlorate, which readily crystallized, was filtered off and washed with acetone. One recrystallization from methanol or from water served to yield a pure compound.

---

* *All melting points are corrected.*

The filtrate was concentrated somewhat and treated with ethyl acetate until the incipient turbidity just disappeared on mixing. The perchlorate, which then crystallized, was filtered off, washed with ethyl-acetate–acetone, and redissolved in acetone. A small amount of undissolved lycopodine perchlorate was filtered off and the concentrated filtrate treated with ethyl acetate. The complanatine perchlorate thus obtained melted sharply at 194° C. It is moderately soluble in hot water and crystallizes in brilliant polyhedra from this solvent. Yield, 8 gm. It contains one molecule of water of crystallization, which is only slowly lost at 110° (2mm.) and rapidly reabsorbed on exposure to air. Found: C, 54.55, 54.41; H, 8.48, 8.16%. Calc. for $C_{18}H_{31}ON \cdot HClO_4 \cdot H_2O$: C, 54.61; H, 8.60%.

The free base was regenerated by treating an aqueous suspension of the perchlorate with ammonia and shaking with ether. The washed solution on evaporation to a small volume deposited colourless needles, which, when washed with ether and recrystallized from acetone-ether, melted sharply at 169° C. Found: C, 77.61; 77.21; H, 11.31, 10.97; N, 5.05%. Calc. for $C_{18}H_{31}ON$: C, 77.98; H, 11.19; N, 5.05%.

Alkaloid L2

The acetone–ethyl-acetate mother liquor from which the lycopodine and the complanatine had been obtained was diluted with water, boiled to expel organic solvents, and filtered while hot. The cooled solution deposited a sparingly soluble perchlorate which, when recrystallized twice more from hot water, was obtained in brilliant stout prisms that melted sharply and without decomposition at 231° C. The perchlorate of alkaloid L2 thus obtained did not lose any weight when heated at 110° (1 mm.) for five hours. Found: C, 55.39; 55.24; H, 7.82, 7.72; N, 3.64%. Calc. for $C_{18}H_{29}O_2N \cdot HClO_4$: C, 55.17; H, 7.66; N, 3.58%.

A small portion of the salt was decomposed with aqueous sodium hydroxide in the presence of purified ether. The washed solution was evaporated to dryness and the residue recrystallized from purified pentane in which it is moderately soluble. Colourless flat prisms of alkaloid L2 melting sharply at 97° C. were thus obtained. Found: C, 74.55; H, 10.09; N, 4.91%. Calc. for $C_{18}H_{29}O_2N$: C, 74.23; H, 9.97; N, 4.81%.

Alkaloid L3

The free bases were regenerated from the aqueous mother liquors from alkaloid L2 and reconverted to perchlorates in concentrated aqueous solution, which on cooling deposited an oily perchlorate. This was washed with cold water by decantation, and it then slowly became crystalline. When it was recrystallized twice from hot water it consisted of brilliant colourless elongated plates that melted sharply at 246° C. Found: C, 55.50, 55.26; H, 8.10, 7.85; N, 3.55%. Calc. for $C_{18}H_{31}O_2N \cdot HClO_4$: C, 54.90; H, 8.13; N, 3.55%.

Alkaloid L4

The aqueous mother liquor from the above perchlorate was concentrated somewhat, filtered (charcoal), and cooled. The perchlorate, which slowly separated, was recrystallized twice from hot water. It was then obtained in pearly plates that melted sharply at 225° C. Found: C, 55.97, 56.17; H, 8.39; 8.12; N, 4.12%. Calc. for $C_{16}H_{27}N . HClO_4 . \frac{1}{2}H_2O$: C, 56.06; H, 8.47; N, 4.09%. At 130° C. the substance lost 3.25% of its weight; $\frac{1}{2}H_2O$ requires 2.63%.

Alkaloid L5

The fraction, b.p. 175 to 185° C. (2 mm.) was redistilled and a fraction boiling at 196° (2 mm.) collected separately. It was dissolved in hot dilute perchloric acid and the filtered (charcoal) solution cooled. The crystals, which separated in the course of several days, were recrystallized from hot water; they were obtained in brilliant colourless polyhedra that melted with slight previous darkening at 282° C. Found: C, 55.53, 55.45; H, 8.32, 7.77; N, 6.76, 7.19%. Calc. for $C_{18}H_{28}O_2N_2 . HClO_4$: C, 55.61; H, 7.64; N, 7.21%. There was no loss in weight at 110° (1 mm.). A further small amount of this perchlorate was obtained from the undistilled residue from which the obscurine had been crystallized. In this case the salt was recrystallized from hot methanol, in which it is only sparingly soluble. The melting point of this perchlorate (L5) is close to that of lycopodine perchlorate. It is therefore of interest to note that a mixture of the two salts was completely liquid at 260° C. Other perchlorates that melt at temperatures reasonably close to each other have been mixed, and in all cases a substantial lowering of melting points has been observed.

Obscurine (L6)

The undistilled residue was dissolved in hot aqueous oxalic acid and the filtered solution extracted with ether. It was then basified with ammonia and the liberated bases were taken up in a large volume of ether. The washed ether solution was evaporated to dryness and the residue dissolved in methanol. The small crop of crystals (0.05 gm.) that separated in the course of several days was filtered off (m.p. 280° C.) and recrystallized from chloroform-methanol, in the latter of which it is sparingly soluble. Colourless needles of obscurine were thus obtained which melted at 282° C. either alone or in admixture with a specimen of alkaloid similarly obtained from *L. obscurum*. Found: C, 74.50, 74.92; H, 9.64, 9.55; N, 9.66, 9.76%. Calc. for $C_{18}H_{28}ON_2$: C, 75.00; H, 9.72; N, 9.72%.

The perchlorate was recrystallized from acetone-ethyl-acetate; it melted with some previous decomposition at 299° C. It is readily soluble in methanol, acetone, and water. The analyses indicate that both nitrogens are basic and one molecule of water was lost at 130° (1 mm.). Found: C, 42.45; H, 6.65; N, 5.08; H_2O, 3.12%. Calc. for $C_{18}H_{28}ON_2 . 2HClO_4 . H_2O$: C, 42.61; H, 6.31; N, 5.52; H_2O, 3.55%.

Nicotine

The low boiling fraction consisted of a colourless oil with a very strong odour of nicotine. It was dissolved in methanol and treated with an excess of picric acid. The sparingly soluble picrate, which crystallized at once, melted at 225° C. It was recrystallized from hot methanol, and it then melted at 226° C. either alone or in admixture with an authentic specimen of nicotine dipicrate. Calc. for $C_{22}H_{20}O_{14}N_8$; N, 18.06%. Found: N, 18.10%.

The fraction of the same boiling point from *Equisetum arvense* was treated in the same manner, and it yielded nicotine dipicrate of equal purity.

The nicotine was regenerated from the picrate and converted to the dipicrolonate, which, when recrystallized from aqueous acetone, melted at 228° C. either alone or in admixture with a specimen of known authenticity. It is estimated that nicotine was present to the extent of 2 p.p.m.

It may be noted that repeated attempts to prepare crystalline picrates from the other *Lycopodium* bases and particularly from lycopodine yielded only sparingly soluble resins.

Hydrolysis of Water Insoluble Polysaccharide

One kilo of the plant material that had been extracted with methanol was soaked in 5 litres of 1% hydrochloric acid overnight. The mixture was filtered and the residue washed with water until the filtrate gave only a slight opalescence with silver nitrate. It was then heated under reflux for two hours with 2% sulphuric acid. The aqueous solution was quantitatively freed of sulphuric acid by means of barium hydroxide and then evaporated to a thick syrup *in vacuo*. The residue was extracted with a litre of hot methanol and the filtered solution evaporated once more *in vacuo* to a thin syrup. Methanol was added until further additions produced no more turbidity. The clear solution was evaporated to about 100 cc. and allowed to remain in a cool place for several weeks. The solid crystalline sugar was filtered off, washed with methanol, and recrystallized from a large volume of boiling methanol. There was obtained 8 gm. of colourless, anhydrous *d*-galactose, which melted at 165° C. either alone or in admixture with an authentic specimen. The phenylosazone was recrystallized from methanol, and it melted at 193° C. either alone or in admixture with *d*-galactose phenylosazone.

An attempt to isolate a sparingly soluble phenylhydrazone (fucose, mannose) from the galactose mother liquor was unsuccessful.

References

1. Achmatowicz, C. and Uzieblo, W. Roczniki Chem. 18 : 88-95. 1938.
2. Bödeker, K. Annalen, 208 : 363-367. 1881.
3. Marion, L. Can. J. Research, B, 17(1) : 21-22. 1939.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. JUNE, 1942 NUMBER 6

THE REMOVAL OF COPPER AND CADMIUM IN THE HYDROMETALLURGY OF ZINC[1]

BY G. T. E. GRAHAM[2] AND T. THORVALDSON[3]

Abstract

A study was made of the precipitation, by means of zinc dust, of copper and cadmium from a "normal thickener overflow" solution as obtained in the hydrometallurgy of zinc. The effect of (i) the quantity of zinc dust added, (ii) the initial pH of the solution, (iii) the time of agitation, and (iv) the aeration of the solution were studied. The polarograph was used to follow the changes in the concentration of the solution.

For the effective removal of cadmium, the initial pH of the solution should not be below 3.5. The time of treatment with zinc dust should be controlled within narrow limits and, while the agitation should be effective, it should not cause aeration of the solution. The redissolving of cadmium on prolonged treatment appears to be a typical process of electrolytic corrosion analogous to underwater corrosion of iron in the neutral zone, the rate of redissolving being dependent on the supply of oxygen for depolarization. Similar redissolving of copper does not take place under the conditions studied and, given sufficient zinc dust, only the minimum time of treatment need be controlled.

In the hydrometallurgy of zinc as carried out at the Flin Flon Plant of the Hudson Bay Mining and Smelting Company (1), there is obtained a solution (called "neutral thickener overflow") containing zinc sulphate in high concentration with small quantities of other metals as impurities. A typical assay of this solution gives the following values in grams per litre: Zn, 120; Cu, 0.221; Cd, 0.152; Mn, 0.049; Fe, 0.031; Co, 0.012; As, 0.0008; Mg, 17.6; Ca, 2.52; suspended solids, 1.0. It is essential to remove the major portion of the copper and cadmium present in this solution before it can be electrolyzed to produce zinc of high purity. This is effected by agitation of the liquid with zinc dust in a batch or continuous process until the amounts of copper and cadmium in solution have been reduced to within the permissible limits. The object of this study was to determine the effect of such factors as the proportion of zinc dust used, the time of agitation, and the hydrogen ion concentration (pH) of the solution on the removal of copper and cadmium from the neutral thickener overflow.

[1] *Manuscript received March 2, 1942.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

[2] *Graduate Student, University of Saskatchewan; at the time, the holder of a Bursary under the National Research Council of Canada.*

[3] *Professor of Chemistry and Lecturer in Metallurgy.*

Materials and Experimental Procedure

The neutral thickener overflow (N.T.O.) solution and the zinc dust used were supplied by the Hudson Bay Mining and Smelting Company from their Zinc Plant at Flin Flon. In order to ensure an approximately constant ratio of surface to weight of zinc in different series of experiments, the zinc dust was sieved and the 140 to 200 mesh fraction used (A.S.T.M. Standard). The solution, which for most of the work was of the composition given above, was filtered to remove suspended solids.

The solution which, unless otherwise stated, had an initial pH value of 5.27 was treated with zinc dust in a cylindrical glass jar in two-litre batches and stirred by means of an efficient motor driven glass stirrer. All the experiments were carried out in a thermostat at 40.0° C. ± 0.1°, this temperature being chosen so as to conform to plant conditions at Flin Flon. Samples of the liquid for analysis were removed by means of a 100 ml. pipette, the tip of which was fitted with a glass wool filter. This effected complete and rapid separation of the liquid from the suspended solids. All pH measurements were made at 21° C. with a Leeds and Northrup Universal pH Indicator, using a glass electrode. The results were reproducible within a pH of ±0.02.

The Determination of Copper and Cadmium

The selection of a suitable method for the rapid and accurate determination of copper and cadmium in the N.T.O. solution before and after the treatment with zinc dust presented some difficulty. A suitable method must be capable of the accurate determination of these substances in concentrations varying from that originally present in the N.T.O. (220 mg. of copper per litre and 150 mg. of cadium per litre) down to about one milligram per litre in presence of 120 gm. of zinc per litre. A number of methods, electrolytic and colorimetric, were studied and found unsatisfactory before it was decided to use the polarographic method.

This method, originally developed by Heyrovsky (2) and applied to quantitative determinations by him and his co-workers at the Charles University in Prague, is based on the interpretation of current-voltage curves obtained by electrolyzing the unknown solution in a cell with a capillary mercury dropping electrode (tip of about 0.03 mm. inside diameter), dropping at a rate of one drop every two to four seconds, and a stationary pool of mercury as the other electrode. Each electro-reducible substance in the solution produces its own characteristic "wave" on the curve, so that under the optimum conditions it is possible to detect and determine both the species and concentration of several such substances in a solution from a single current-voltage curve. The method is especially suitable for the concentrations of from 10^{-5} to 10^{-2} molar, the attainable accuracy being within about 2% when the concentration is greater than 10^{-4} and within 10% when it is between 10^{-4} and 10^{-5} molar. For a detailed discussion of the method and its applications, the reader is referred to a paper by Kolthoff and Lingane (3).

The Polarographic Equipment

Only a few of the essential details of the equipment will be given. The electrolytic cell was of Pyrex glass, of 55 ml. capacity, and was designed so as to facilitate the introduction and removal of the test solution by means of a side-tube without disturbing the dropping electrode. A saturated calomel reference electrode was attached by means of a ground glass joint to a side-tube of the cell, the saturated potassium chloride and the test solution being separated by a porous ground-glass plug. A stream of nitrogen purified by alkaline pyrogallol, which was introduced into the cell near the bottom, was used to remove all oxygen from the test solution before the electrolysis. A trap was provided for the escape of the nitrogen from the cell.

The variable potential was obtained from a battery by using two potentiometer-type rheostats connected in series, one of 1000 ohms resistance for coarse adjustment and one of 10 ohms for fine adjustment. The galvanometer, which was critically damped, had a sensitivity of 0.0023 micro amperes per millimetre scale division and its shunt consisted of a precision resistance box. A Leeds and Northrup student type potentiometer and Weston standard cell for calibration were also used. A dial-type double pole switch was installed so that the following potentiometric measurements could be readily made.

1. Potential drop across the resistance box for calculating the current as a check on the galvanometer measurements.
2. The total applied potential between the dropping electrode and the stationary mercury pool.
3. The potential of the dropping electrode against the calomel reference electrode.
4. The potential of the quiet mercury pool against the calomel electrode.

At the beginning of each run the dropping time was adjusted to 3.00 sec. by means of a system of levelling bulbs. When great pains were taken in the purification of the mercury, the dropping electrode worked well during several months of use. When it began to show erratic behaviour it was found preferable to make and recalibrate a new one rather than try to clean the tip.

The polarographic measurements were made at 21° C. The temperature of the room itself fluctuated only slightly from this temperature.

Calibration of the Polarograph

The polarograph was calibrated with a series of solutions of known concentration of which the copper content varied from 5 to 250 mg. per litre, and the cadmium from 5 to 150 mg. per litre, whereas the concentration of zinc remained constant at 120 gm. per litre, all present as the sulphates. In order to eliminate maxima on the current-voltage curves, 10 drops (0.30 ml.) of a 0.2% methyl red solution was added in each case to 55 ml. of the test solution, and a resistance of 9000 ohms was used in series with the cell. For solutions containing copper and cadmium in the higher concentrations, a shunt of 9 ohms was used with the galvanometer, whereas for the lower concentrations this was changed to a shunt of 150 ohms to increase the height of the wave and the accuracy of the wave height determination. Fig. 1 gives an example of a current-voltage curve for a solution containing 150 mg. of copper per litre, 125 mg. of cadmium per litre, and 120 gm. of zinc per litre, using a 9 ohm shunt. The half-wave potential for copper under the conditions of the experiments was found to be −0.02 volts and for cadmium, −0.61 volts, with respect to the saturated calomel electrode.

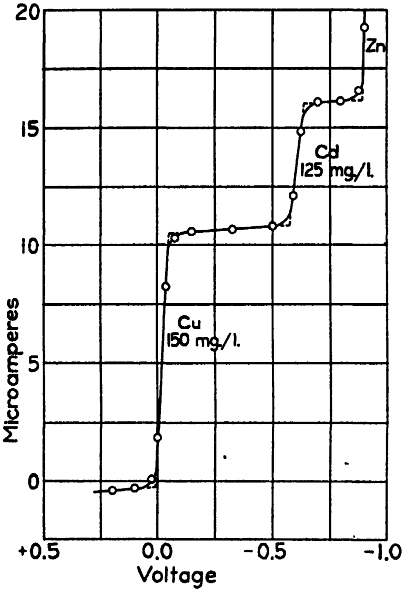


FIG. 1. *Current-voltage curve for copper and cadmium.*

Two methods were used for estimating the wave height and thus for determining the concentration of the electro-reducible substance in solution. One is illustrated in Fig. 1, namely, drawing the best straight line through each "plateau" and then measuring the differences in height. The other is the method of Müller and Petras (4), which reduces the necessary measurements of the current to that obtained for two fixed voltages. A linear calibration curve is obtained by plotting the differences between these two values for solutions of various known concentrations against the concentration. Using the 9 and 150 ohm shunts the concentrations of copper corresponding to 1 mm. of wave height were found to be 1.83 and 0.156 mg. of copper per litre, respectively. The corresponding values for cadmium were 3.30 and 0.250 mg. per litre, respectively.

Experimental Results

Effect of Amount of Zinc Dust Added to the N.T.O. and of Time of Agitation on the Removal of Copper and Cadmium and on the Final pH of the Solution

Fig. 2 shows the effect of agitation time on the deposition of copper from the N.T.O. solution for runs with zinc dust additions varying from 0.125 to 0.500 gm. per litre. It is evident that addition of 0.125 gm. of zinc dust per litre is insufficient to remove more than about half of the copper from solution; the addition of 0.250 gm. of zinc dust per litre reduces the copper to about 5 mg. per litre, while additions of 0.375 gm. per litre and 0.500 gm. per litre reduce the copper content to less than 1 mg. per litre in 50 and 35 min., respectively.

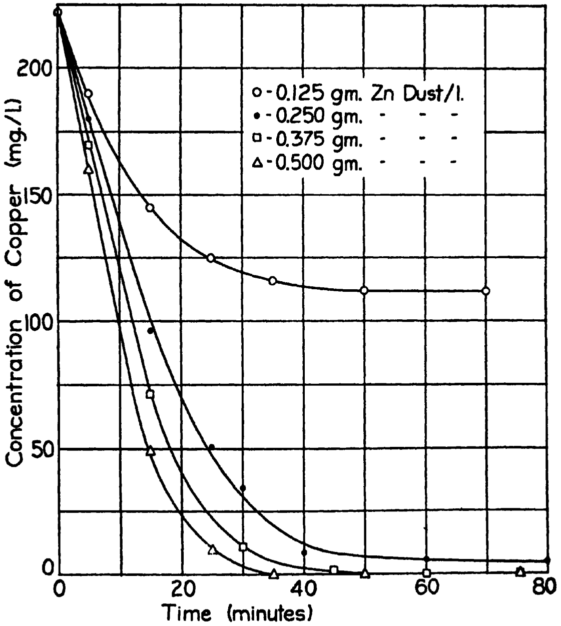


FIG. 2. *Effect of amount of zinc dust added and agitation time on the precipitation of copper.*

The corresponding graphs (Fig. 3) showing the effect of time of agitation and the amount of zinc dust added on the deposition of cadmium indicate that with the 0.125 and 0.250 gm. additions of zinc per litre of solution there is only a slight temporary deposition of cadmium and that redissolving of this soon takes place. With the 0.375 gm. per litre addition the precipitation of cadmium is somewhat greater, but partial redissolving occurs rapidly, this effect continuing more slowly after about 40 min. The 0.500 gm. per litre addition of zinc dust reduces the cadmium concentration to a minimum of 7 mg. of cadmium per litre in 45 min. and, after this, redissolving of cadmium occurs at a very slow rate. In a later series of experiments it was found that addition of 0.65 gm. of zinc dust reduced the cadmium to 2 mg. per litre.

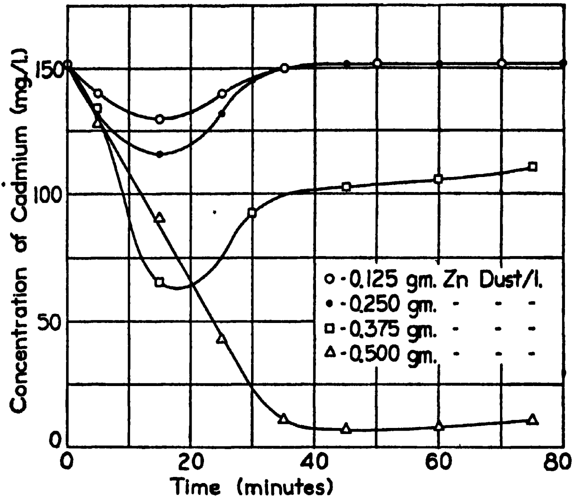


FIG. 3. *Effect of amount of zinc dust added and agitation time on the precipitation of cadmium.*

Fig. 4 gives the corresponding curves showing the effect of the amount of zinc dust added and the agitation time on the pH of the N.T.O. solution. Starting with a solution of pH = 5.27, the addition of zinc dust raises the pH progressively, the value in each case reaching a maximum in about 40 minutes. The maximum value for the addition of 0.500 gm. of zinc dust per litre is pH = 5.60, which is the same within experimental error as the value for the addition of 0.375 gm. of zinc dust per litre.

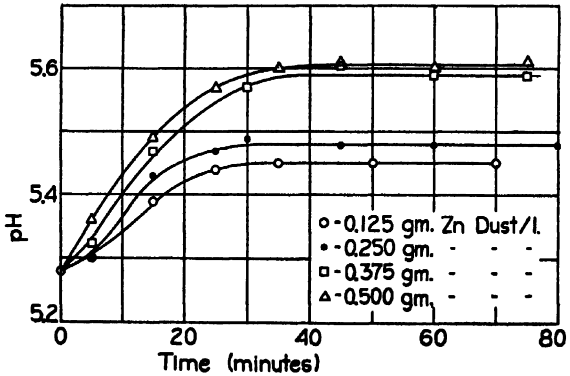


FIG. 4. *Effect of amount of zinc dust added and agitation time on the pH of the N.T.O. solution.*

Considering the above results, it was decided to fix the time of agitation of the N.T.O. solution with zinc dust at 45 min. in all further experiments.

Replicate determinations of the above-mentioned curves agreed very well as to the horizontal portions and as well as could be expected along the vertical portions where time is an important factor.

Fig. 5 shows the effect of the amount of zinc dust added on the precipitation of the cadmium from the N.T.O. solution. The time of agitation in all cases was 45 min. It is apparent that there is no permanent precipitation of cadmium if less than 0.250 gm. of zinc dust per litre is added and that an addition of 0.500 gm. per litre is necessary to reduce the cadmium content to 7 mg. per litre.

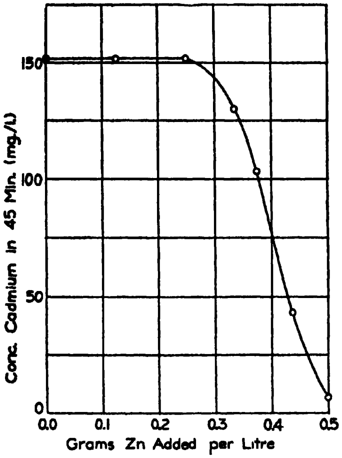


FIG. 5. *Effect of amount of zinc dust added on final concentration of cadmium.*

The Effect of the Initial pH of the N.T.O. Solution

Fig. 6 gives the effect of the initial pH of the N.T.O. solution on the precipitation of cadmium at 40° C. on addition of 0.5 gm. of zinc dust per litre and an agitation time of 45 min. It shows that, provided the initial pH of the solution is between the limits 5.1 and 3.6, there was no noticeable effect on the final concentration of cadmium. Below pH of 3.5 there is a rapid increase in the cadmium remaining in the solution at the end of 45 min., and at a pH of 2 the final concentration of cadmium reaches 96 mg. per litre (initial, 152 mg. per litre). When the initial pH was below 3.0, bubbles of hydrogen came off at such a rate as to make the solution appear opalescent*. Initial pH values down to 2 did not affect the precipitation of copper materially.

---

* *In a private communication Mr. S. P. Lowe, Superintendent of Research, Hudson Bay Mining and Smelting Company, states that hydrogen is evolved from the solution during the treatment with zinc dust providing the pH is below 6. The noticeable evolution of hydrogen gas at the higher pH values under plant conditions is probably due to the fact that the proportion of zinc dust used in plant practice is several times the largest amount used in our experiments. The large excess is considered necessary in order to remove arsenic, antimony, and cobalt, the presence of which lowers the current efficiency during the deposition of the zinc.*

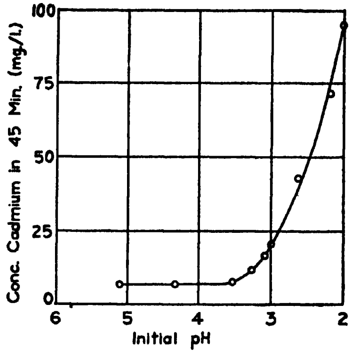


FIG. 6. *Effect of the initial pH of the N.T.O. solution on the precipitation of cadmium.*

The Effect of Air on the Removal of Cadmium and Copper

It is well known in practice that during the later stages of the agitation of the N.T.O. solution with zinc dust, cadmium tends to redissolve in the liquid. (This effect is illustrated in all the curves of Fig. 3.) The authors are not aware that any explanation of this phenomenon has been proposed. As the effect of aeration on the rate of underwater corrosion of base metals, such as iron, in the neutral and acid zone is well known, an experiment was made to determine the effect of bubbling air through the N.T.O. solution after the

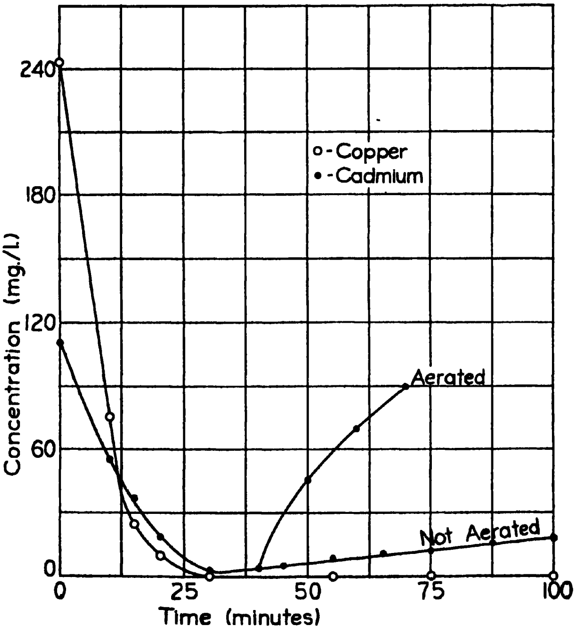


FIG. 7. *Effect of aeration of the N.T.O. solution on the redissolving of cadmium.*

minimum cadmium content of the solution had been reached. The solution was treated with 0.65 gm. of zinc dust per litre at 40° C. in the usual way. The copper content was reduced to zero and the cadmium content to a minimum of 2 mg. per litre. In a second run a rapid current of air was passed through the solution after the initial 40 min. and the determination of copper and cadmium continued at intervals. Fig. 7 shows the curve obtained for the copper and cadmium content of the solution compared with the normal curve obtained without aeration. This shows very rapid redissolving of cadmium in the aerated liquid, the concentration reaching 90 mg. per litre after aeration for 30 min. (initial, 110 mg. of cadmium per litre). No redissolving of copper was observed.

Discussion

Assuming that we are dealing with the direct displacement of copper and cadmium in solution by zinc, the addition of 125 mg. of zinc dust (100% pure) per litre should precipitate 55% of the copper present, as against 50% actually precipitated, an efficiency of 90% of the theoretical at the end of 50 min. agitation. The 250 mg. addition of zinc dust represents about 10% in excess of the requirements for precipitating all the copper, and as at the end of 60 min. 98% of the copper and none of the cadmium remains precipitated, the efficiency is about 89% of the theoretical. For the addition of 375 mg. of zinc dust the precipitation in 60 min. represents 100% of the copper and 30% of the cadmium present which is only 68% of the theoretical, although if one considers the points of maximum precipitation of copper (100%) and cadmium (57%) separately the efficiency is 74% of the theoretical. Similarly, for 500 mg. addition of zinc dust the precipitation in 45 min. represents 100% of the copper and 95.4% of the cadmium, giving an efficiency of 62.5%.

The behaviour of the cadmium is in agreement with what would be expected on the basis of the electrochemical theory of corrosion (5, pp. 21–41; 6). The single electrode potentials involved are: copper = +0.34; H = ±0.00; cadmium = −0.40; and zinc = − 0.76 volts. Considering the three metals, we have the possibility of three electrical couples, Cu–Zn (1.1 volts), Cd–Zn (0.36 volts) and Cu–Cd (0.74 volts). The initial effect of adding zinc dust to a solution containing copper and cadmium is to deposit both the metals on the zinc dust, the deposition of copper predominating. Soon, however, the copper–cadmium couple operates, with the result that the latter dissolves and no further effective precipitation of cadmium occurs. If there is insufficient zinc dust to precipitate all the copper, the cadmium already precipitated will redissolve during the later stages of the precipitation of copper. This is illustrated by the two smallest additions of zinc dust (Figs. 2 and 3). With the two larger proportions of zinc dust, the copper is completely precipitated, and the slow redissolving of cadmium cannot be due to the replacement of copper in the solution by cadmium. Under the conditions of the writers' experiments, hydrogen gas is not evolved in any considerable quantities during the precipitation of cadmium unless the pH is quite low (below about 3 to 3.5), i.e., unless the hydrogen ion concentration is high. A factor preventing the evolution of hydrogen during the precipitation of cadmium is the high overvoltage of hydrogen on copper (which on polished copper varies from 0.5 to 1.2+ volts), while the overvoltage for the deposition of metal on metal is small. Thus hydrogen behaves as if it were more anodic than cadmium, and the latter may be almost completely replaced by zinc on the acid side of the neutral point. The effect of the hydrogen ion concentration on the removal of cadmium is illustrated in Fig. 6.

The slow redissolving of cadmium shown in the 0.375, 0.500, and 0.65 gm. additions of zinc (see Figs. 3 and 7) is apparently due to depolarization by oxygen. The film of hydrogen, which plates out on the precipitated copper in contact with precipitated cadmium through the displacement of hydrogen ions by cadmium, prevents further action. This film, which may be atomic and is at any rate quite reactive, is removed by the oxygen in solution, and the rate of redissolving of cadmium is therefore determined by the rate at which oxygen is supplied; hence the rapid increase in the redissolving of cadmium during aeration (Fig. 7). When the hydrogen ion concentration is high enough, molecular hydrogen is evolved and the process continues spontaneously in the absence of oxygen.

Acknowledgments

The authors are indebted to Mr. S. P. Lowe, Superintendent of Research of the Hudson Bay Mining and Smelting Company, for suggesting this problem, for supplying the N.T.O. solution and the zinc dust, as well as for constructive criticism of the preliminary manuscript. They also wish to thank Dr. J. W. T. Spinks and Mr. M. R. Foran for helpful suggestions in connection with the experimental work.

References

1. Carr, J. D. and Reikie, M. K. T. Trans. Can. Inst. Mining Met. 38 : 287-310. 1935.
2. Heyrovsky, J. Phil. Mag. (Ser. 6) 45 : 303-315. 1923.
3. Kolthoff, I. M. and Lingane, J. J. Chem. Revs. 24(1) : 1-94. 1939.
4. Müller, R. H. and Petras, J. F. J. Am. Chem. Soc. 60(12) : 2990-2993. 1938.
5. Speller, F. N. Corrosion. McGraw-Hill Book Company, Inc., New York and London. 1926.
6. Whitney, W. R. J. Am. Chem. Soc. 25(4) : 394-406. 1903.

THE DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE[1]

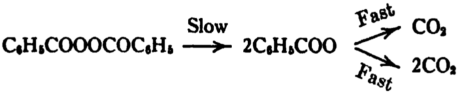
By J. H. McClure[2], R. E. Robertson[3], and A. C. Cuthbertson[4]

Abstract

A kinetic study has been made of the decomposition of benzoyl peroxide in benzene. Kinetic data for this study have been obtained from three separate sets of measurements. Rate measurements from evolved carbon dioxide and direct iodometric measurements of peroxide are in good agreement. Alkalimetric determinations of the product, benzoic acid, have also been made during the course of the reaction.

Gravimetric determinations show that the total evolved carbon dioxide from the reaction is a function of the temperature, and indicate that the mechanism involves two parallel fast reactions, one of which evolves one mole of carbon dioxide per mole of peroxide and the other two moles of carbon dioxide per mole of peroxide. The latter reaction predominates at higher temperatures.

A kinetic analysis is included and provides for a slow reaction involving the rupture of the peroxide bond, followed by free radical reactions.



$$C_6H_5COOOCOC_6H_5 \xrightarrow{\text{Slow}} 2C_6H_5COO \left< \begin{array}{l} \xrightarrow{\text{Fast}} CO_2 \\ \xrightarrow{\text{Fast}} 2CO_2 \end{array} \right.$$

The secondary free radical reactions would probably form hydrogen radicals, but there is evidence to support the view that these hydrogen radicals are not eliminated by mutual termination.

The reaction is first order and the energy of activation was found to be 31,000 cal. per mole.

Introduction

In this investigation, which deals with the decomposition of benzoyl peroxide in benzene, an attempt will be made to formulate a kinetic mechanism by which the reaction takes place. The obvious complexity of the reaction has made it advisable to obtain measurements not only for the rate of disappearance of the peroxide, but also for the rate of formation of the products, notably carbon dioxide and benzoic acid. Other investigators (1–3, 6, 8–13, 27), with two exceptions (4, 18), have studied the decomposition of benzoyl peroxide not from the standpoint of rate but by analysis of the end-products obtained after refluxing the peroxide in various solvents for protracted periods of time, or by heating the solid peroxide with sand as a diluent.

As early as 1864, Brodie (2, 3) found that benzoyl peroxide mixed with sand decomposed to yield one mole of carbon dioxide per mole of peroxide. Orndorff and White (21) noted the decomposition of benzoyl peroxide in boiling benzene with the liberation of carbon dioxide, while Lippmann (19) found that no reaction took place until the solution was heated in a closed tube to a temperature somewhat over 100° C. The latter obtained one mole of carbon dioxide per mole of peroxide, benzoic acid, benzoic anhydride, and diphenyl. Diphenyl was produced when the compound was heated with sand, and he concluded that the benzene was an inert medium.

---

[1] *Manuscript received in original form March 2, 1942, and as revised, April 27, 1942. Contribution from the Department of Chemistry, Mount Allison University, Sackville, N.B.*

[2] *Instructor, 1940–1941.*

[3] *Instructor, 1941–1942.*

[4] *Professor of Chemistry.*

In the years following 1924, Gelissen and Hermans (8–13) and later Böeseken (1) carried out many investigations on the decomposition of diacyl peroxides in ordinary solvents. In the case of benzoyl peroxide their earlier investigations led them to assume that benzene or other solvents reacted with the benzoyl peroxide according to the following scheme, which involved a main and side reaction.

$$\text{I}\quad C_6H_5COOOCOC_6H_5 + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5C_6H_5 + CO_2 \qquad \text{Main}$$

$$\text{II}\quad C_6H_5COOOCOC_6H_5 + C_6H_6 \longrightarrow C_6H_5COOC_6H_5 + C_6H_6 + CO_2 \qquad \text{Side}$$

It is to be noted that according to this mechanism one mole of carbon dioxide is evolved per mole of benzoyl peroxide. The analysis of the end-products of the reaction showed the following substances present:— benzoic acid (partly in the form of an ester), 37.6%; diphenyl, 16.7%; phenyl-benzoate, 1.67%; quaterphenyl, 2.2%; a residue amounting to 29.2% (having a composition: C, 80%; H, 6%; O, 14%); and a small quantity of terphenyl. In addition 20.8% of carbon dioxide was evolved. It will be seen later that the assumption that this percentage corresponds to one mole of carbon dioxide per mole of peroxide is probably in error. Experiments carried out by us show that had the reaction been run to completion rather than for seven hours, the percentage of carbon dioxide would have varied even more strikingly from their theoretical value of 18.2%. In another communication (15) the above authors found that when benzoyl peroxide was heated above its melting point either with or without a solvent the decomposition proceeded according to the following scheme:

$$C_6H_5COOOCOC_6H_5 \longrightarrow C_6H_5C_6H_5 + 2CO_2$$

The same authors, as well as others (26), proved that benzene participated in the reaction because di-*p*-chlorobenzoyl peroxide, on decomposition in benzene yielded *p*-chlorobiphenyl rather than *p,p*-dichlorobiphenyl. Similarly *m,m*-dinitrobenzoyl peroxide gave 3-nitrodiphenyl rather than 3,3-dinitrodiphenyl. Hey (16) gives further proof of the reaction of the peroxide with the solvent.

Some years later Böeseken and Hermans (1) summarized the possible reactions as follows:

$$\text{I}\quad C_6H_5COO\,.\,OCOC_6H_5 \longrightarrow C_6H_5C_6H_5 + 2CO_2$$

$$\text{II}\quad C_6H_5COO\,.\,OCOC_6H_5 \longrightarrow C_6H_5COOC_6H_5 + CO_2$$

$$\text{III}\quad C_6H_5COO\,.\,OCOC_6H_5 \longrightarrow C_6H_5C_6H_4COOH + CO_2$$

$$\text{IV}\quad C_6H_5COO\,.\,OCOC_6H_5 + C_6H_6 \longrightarrow \underset{\displaystyle\downarrow \atop \displaystyle C_6H_5COOH + CO_2}{C_6H_5COO\,.\,OCOH} + C_6H_5C_6H_5$$

According to this scheme, the main path of the decomposition proceeds by Reactions I and II. Proof of the presence of phenylbenzoic acid has been established by Wieland (27).

The question whether a free radical mechanism is involved has been discussed by Wieland and co-workers (27) and by Hey and Waters (17) and others (24). The first have maintained that the presence of free radicals was both unlikely and unnecessary to explain the decomposition of peroxides. The same opinion was also held by Reynhart (22) and implied by Böeseken and Hermans (1). Hey and Waters (17) do not consider the evidence against the presence of free radicals conclusive, and propose that the initial stage of decomposition is the formation of free radicals as set forth below:

$$C_6H_5COOOCOC_6H_5 \longrightarrow C_6H_5^{\bullet} + C_6H_5COO^{\bullet} + CO_2 ,$$

followed by such reactions as:

$$\begin{aligned}&C_6H_5COO^{\bullet} + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5^{\bullet}\\&C_6H_5^{\bullet} + C_6H_6 \longrightarrow C_6H_5C_6H_5 + H^{\bullet}\\&C_6H_5^{\bullet} + C_6H_5C_6H_5 \longrightarrow C_6H_5C_6H_4C_6H_5 + H^{\bullet}\\&C_6H_5COO^{\bullet} + H^{\bullet} \longrightarrow C_6H_5COOH\\&\text{etc.}\end{aligned}$$

The reactivity of the phenyl radical is well known, and it is expected that if it were produced a reaction with solvent molecules would occur. Certainly the formation of ter- and quater-phenyl could easily be explained on the basis of the production of free phenyl radicals.

Although this reaction is obviously complicated an attempt will be made in what follows to make a kinetic analysis, bearing in mind certain facts which a preliminary study indicated were fundamental. So far as the measurement of the rate of the reaction is concerned, this may be accomplished either by titration of liberated iodine with thiosulphate according to the method of Gelissen and Hermans (14); or the evolution of carbon dioxide will provide a continuous method if a simple stoichiometric relation can be found between the concentration of benzoyl peroxide and evolved carbon dioxide at any time. From the mechanisms suggested one is led to believe that one mole of carbon dioxide is evolved for every mole of benzoyl peroxide decomposed. Careful measurements indicate, however, that the number of moles of carbon dioxide evolved is a function of the temperature; that is to say, at a temperature in the vicinity of 65° C., one mole of carbon dioxide is produced per mole of peroxide while at the temperature of boiling benzene, about one and one-half moles of carbon dioxide are evolved. These facts need to be incorporated into any kinetic mechanism. It is essential to express the same mechanism in terms of more than one set of measurements, i.e., in terms of evolved carbon dioxide, thiosulphate titres of the peroxide and perhaps alkali titres of the benzoic acid. If all these data can be satisfactorily correlated, it can confidently be felt that it approximates the truth.

A difficulty will be experienced in the study of this reaction unless the reactants are of a high degree of purity. This difficulty is substantiated by some of the earlier investigators (8). Brown (4) finds a short induction period for this reaction. We found none in experiments where carefully purified materials were used, though our mechanism does not exclude the possibility of one. The fact that the rate is, to a good approximation, first order indicates that if an induction period is present it is very short and relatively unimportant.

Kinetic Analysis

The increase per mole in the evolution of carbon dioxide with rising temperature is explained by assuming that there is a slow initial decomposition of the benzoyl peroxide molecule into two benzoyl radicals (17; 25, p. 776), followed by two fast parallel reactions yielding one and two moles of carbon dioxide respectively.

$$\begin{tikzcd}[row sep=tiny] & & \text{CO}_2\text{ products} & \text{Path 1} \\ (1)\ C_6H_5COOOCOC_6H_5 \arrow[r, "\text{Slow}", "k_1"'] & 2C_6H_5COO \arrow[ur, "k_2"] \arrow[dr, "k_3"'] & & \\ & & 2\text{CO}_2\text{ products} & \text{Path 2} \end{tikzcd}$$

The initial decomposition may be followed by such fast free radical reactions as:

(2) $C_6H_5COO^{\cdot} + C_6H_5COO^{\cdot} \longrightarrow C_6H_5COOC_6H_5 + CO_2$ Path 1

(3) $2C_6H_5COO^{\cdot} + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5C_6H_5 + CO_2$

$C_6H_5COO\,.\,OCOC_6H_5 \longrightarrow 2C_6H_5COO^{\cdot} \longrightarrow 2CO_2 + 2C_6H_5^{\cdot}$ Path 2 (i)

$C_6H_5^{\cdot} + C_6H_6 \longrightarrow C_6H_5C_6H_5 + H^{\cdot}$ (ii) Collision with solvent (*a*)

*$C_6H_5^{\cdot} + C_6H_6 \longrightarrow C_6H_6 + C_6H_5^{\cdot}$ (ii) Collision with solvent (*b*)

$C_6H_5^{\cdot} + C_6H_5C_6H_5 \longrightarrow C_6H_5C_6H_4C_6H_5 + H^{\cdot}$ (iii)

Free Radical Termination Reactions

$H^{\cdot} + C_6H_5^{\cdot} \longrightarrow C_6H_6$ (iv) (*a*)

$H^{\cdot} + H^{\cdot} \longrightarrow H_2$ (iv) (*b*)

$C_6H_5^{\cdot} + C_6H_5^{\cdot} \longrightarrow C_6H_5C_6H_5$ (iv) (*c*)

If M is the concentration of peroxide at any time t, the rate may be expressed:

$$\frac{-dM}{dt} = k_1 M.$$

If x be the fraction of a mole of peroxide changing by Path 2, then

$$\frac{x}{1 - x} = \frac{k_3}{k_2},$$

and C_t, the total number of moles of carbon dioxide evolved at any time t, will be:

$$= (1 + x)\,(A + M),$$

where A is the initial peroxide concentration. Substituting for x

$$C_t = \frac{(2k_3 + k_2)}{(k_3 + k_2)}\,(A - M) = y\,\frac{(2 + K)}{(1 + K)},$$

---

* *Transfer reaction.*

where $K = \frac{k_2}{k_3}$ and y is the amount of peroxide decomposed at time t. Hence the total evolved carbon dioxide is expressed by

$$C_\infty = \frac{2 + K}{1 + K} \cdot A.$$

This permits the evaluation of K and hence y at any time t. Our original kinetic equation in terms of evolved carbon dioxide now becomes

$$\frac{dy}{dt} = k_1 (A - y).$$

The iodometric titration of the peroxide at any time t will yield directly the value of M. Thus we have available two separate methods for determining the value of k_1. The results so obtained at three temperatures are given in Table IV. The rate of production of benzoic acid may be controlled by k_1; hence values of k_1 calculated from alkalimetric determinations of the acid are included.

Experimental

Materials

Benzene: Analar benzene from B.D.H. was kept over metallic sodium and redistilled before use.

Benzoyl peroxide: This product was obtained from B.D.H. and contained 25% of water. It was dissolved in chloroform and twice precipitated by pouring into twice the volume of methyl alcohol according to the method suggested by Gattermann (7, p. 126).

Acetone: In iodometric determinations of the peroxide it is necessary to use pure acetone (5, 14) since the commercial product will frequently free iodine from potassium iodide. The titration medium should be as low in water content as the experimental conditions will permit, otherwise low titration values will be obtained.

Apparatus

Reactions were carried out in an all-glass apparatus. In the volume measurements of carbon dioxide care was exercised in the design of the apparatus so that the volume above the liquid phase was small. The carbon dioxide evolved was collected over mercury in a gas burette so constructed that small volumes measured during the initial stages of the reaction were read with an accuracy comparable to that obtained with larger volumes in the later stages. For the titration experiments a 250 ml. distilling flask with a sealed-on condenser (30 cm. long) was used. Samples were removed through a capillary tube immersed in the solution. Gravimetric determinations were carried out by attaching to the upper end of the condenser a trap immersed in a freezing mixture, followed by a standard carbon dioxide absorption train.

Procedure

In experiments involving the evolution of carbon dioxide a measured quantity of benzene was placed in the apparatus and allowed to stand for 15 min. to ensure that it had reached the correct temperature. The glass mercury seal was then raised and a small quantity of benzoyl peroxide quickly added. Following the replacement of the mercury seal, a three-way stopcock attached between the reflux condenser and the measuring tube was allowed to remain open to the air for five minutes in order to permit any trapped air to reach the correct temperature and pressure. In titration determinations, samples were cooled to 25° C. before the 5 ml. samples were pipetted out. Owing to the insolubility of benzoic and phenylbenzoic acid, care was needed to obtain the true end-point, in alkalimetric titrations. Actual tests with phenyl benzoate showed that under the conditions of titration, no appreciable hydrolysis took place.

Data

In Table I are shown typical yields of carbon dioxide per mole of benzoyl peroxide as obtained from measurements of evolved gas.

TABLE I

YIELDS OF CARBON DIOXIDE

Run No.	Temp., °C.	Conc., moles per litre		
		Benzoyl peroxide	CO_2	C_∞/A
13	66	0.0684	0.0732	1.07
14	66	0.112	0.121	1.08
15	66	0.168	0.181	1.07
8	72.5	0.069	0.087	1.25
18	72.5	0.139	0.174	1.25
7	72.5	0.208	0.260	1.25
9	78	0.0690	0.0999	1.45
11	78	0.110	0.167	1.51
12	78	0.166	0.247	1.49

Evidence set forth in Table II shows that the reaction is first order by comparing the times to half-value for varying concentrations of peroxide in benzene at three temperatures.

Some typical kinetic data regarding carbon dioxide evolution, thiosulphate titres, and alkali titres, at three temperatures, and calculated values of k_1 are detailed in Table III. A summary of the above values and ratios of $\frac{k_2}{k_3}$ is set forth in Table IV.

The corresponding yields of carbon dioxide obtained gravimetrically per mole of benzoyl peroxide are given in Table V.

Discussion

The suggestion that benzoyl peroxide decomposes so as to produce free radicals is not new. Arguments both in favour and against this proposal have been cited in the introduction. As Walker and Wild point out (24)

TABLE II

A COMPARISON OF TIMES TO HALF-VALUE

Run	Conc. peroxide, moles/litre	Time to half-value, hr.	
		Calc.	Obs.
Temp., 66° C.			
15	0.168	21.2	20.2
13	0.0684	25.7	27.0
14	0.112	27.4	23.0
Temp., 72.5° C.			
7	0.208	11.2	11.0
8	0.0695	9.6	9.1
18	0.139	10.1	9.8
Temp., 78° C.			
9	0.0690	5.05	4.9
11	0.110	4.9	4.7
12	0.165	5.3	4.3

TABLE III

TYPICAL KINETIC DATA FROM THREE DIFFERENT SETS OF MEASUREMENTS

Run	14		31		32	
Initial conc., moles/litre	0.112		0.140		0.140	
Time, hr.	Vol. CO_2, ml., S.T.P.	$k_1 \times 10^2$, *hr.*$^{-1}$	Titre with 0.101 *N* $Na_2S_2O_3$	$k_1 \times 10^2$, hr.$^{-1}$	Titre with 0.367 *N* $Ba(OH)_2$	$k_1 \times 10^2$, hr.$^{-1}$
Temp., 66° C.						
0	0.0	–	14.30	–	0 0	–
4	7.5	2.46	12.90	2.6	0.90	2.9
7	12.8	2.48	12.05	2.5	1.60	3.40
13	22.2	2.50	10.20	2.6	2.45	3.5
23	37.0	2.71	7.80	2.6	3.90	2.90
28	44.0	2.84	7.05	2.5	4.5	3.0
46.5	62.9	3.3	4.80	2.4	5.9	2.8
∞	80	–	–	–	8.0	–
Temp., 78° C.						
Run	11		29		24	
Initial conc., moles/litre	0.1104		0.140		0.140	
0	0	–	14.30	–	0	–
2	27.0	13.8	11.20	12.5	1.50	10.8
5	56.7	14.1	7.30	13.4	2.90	10.1
7	71.5	14.5	5.45	13.8	3.80	10.8
9	82.0	14.5	–	–	4.5	10.3
12	93.5	13.5	2.6	14.2	5.4	10.3
∞	112	–	–	–	7.30	–

TABLE IV

FIRST ORDER CONSTANTS AND RATIOS OF k_2/k_1 AT THREE TEMPERATURES

Run	k_1, hr.$^{-1}$	$\frac{k_2}{k_1}$
Temp., 66° C.		
13	2.70×10^{-2}	13.2
*14	2.53×10^{-2}	12.2
15	3.13×10^{-2}	11.8
Av. CO_2	2.78×10^{-2}	Av. 12.4
†31 Iodometric	2.45×10^{-2}	
‡32 Alkalimetric	2.76×10^{-2}	
Temp., 72.5° C.		
8	7.20×10^{-2}	2.94
18	6.87×10^{-2}	2.95
7	6.17×10^{-2}	3.08
Av. CO_2	6.74×10^{-2}	Av. 2.99
†Iodometric	5.09×10^{-2}	
‡Alkalimetric	4.97×10^{-2}	
Temp., 78° C.		
9	1.37×10^{-1}	1.23
11	1.41×10^{-1}	0.95
12	1.30×10^{-1}	1.06
Av. CO_2	1.36×10^{-1}	Av. 1.08
†Iodometric	1.35×10^{-1}	
‡Alkalimetric	1.05×10^{-1}	

* *This value is an average k_1, from a larger set of data than presented in Table III.*

† *These values were obtained by titrating iodine freed by potassium iodide from 5 ml. samples of benzoyl-peroxide-benzene solution. There is good reason to believe the value of 5.09×10^{-2} at 72.5° is somewhat low.*

‡ *These values were obtained by titration of the products benzoic and phenyl benzoic acid with barium hydroxide.*

TABLE V

GRAVIMETRIC DETERMINATIONS OF CARBON DIOXIDE

Run	Temp., °C.	Conc. peroxide, gm.	CO_2, gm.	C_∞/A expressed, moles
27	78	1.7857	0.4784	1.47
19	72.5	0.800	0.1773	1.25
31	66	3.5853	0.6980	1.07

the RH scheme suggested by Gelissen and Hermans (8–13) and in modified form by Böeseken and Hermans (1) summarizes in convenient form and comprehensive manner the different kinds of end-products of the thermal decomposition without suggesting the real mechanism through which such products are produced.

On the other hand, the free radical mechanism proposed by Hey and Waters (17) will be in agreement with our experimental data if provision be made for the variation of total evolved carbon dioxide per mole of benzoyl peroxide with temperature. In order to reconcile the characteristics of free radical reactions with the relative slowness of the above decomposition (half-life = 10 hr. at 72.5° C.) it is necessary to postulate a mechanism having two steps.

The first step in the decomposition is concerned with the slow production of free benzoyl radicals. Since the subsequent free radical reactions are very rapid, the rate actually measured (25, p. 776) will be that rate at which the peroxide bond is broken, and, as Rice (23) points out, the minimum value for the activation energy may correspond to the energy required for the rupture of the peroxide bond. Acetyl peroxide has the same kind of a peroxide bond. It is significant therefore that Walker and Wild (24) found the activation energy for the unimolecular decomposition of acetyl peroxide in toluene at 80° C. to be 31,000 cal. per mole, compared with 31,000 cal. per mole found by us from values of k_1 obtained from average carbon dioxide data, Table IV. The energy of activation for benzoyl peroxide in benzene calculated from the data of Kamenskaja and Medwedew (18) at 75° and 85° was found to be 30,000 cal. This may indicate that the rate of bond rupture is nearly independent of the nature of the "R" groups associated with the peroxide linkage.

Since the total moles of carbon dioxide evolved per mole of benzoyl peroxide is a function of the temperature (Fig. 1), there must be two types of secondary reactions. The first, predominating at lower temperatures, yields one mole of carbon dioxide per mole of peroxide, together with benzoic, phenylbenzoic acids and various aryl esters. The second, amounting to 50% of the total at 78° C., yields two moles of carbon dioxide per mole of peroxide together with phenyl radicals which in turn react with solvent and other molecules. The presence of such reactive particles will most easily explain the formation of polyphenyls and higher molecular weight esters found by Gelissen and Hermans.

According to our results data from the evolution of carbon dioxide and alkalimetric titration indicate that at 66° C. Equations (2) and (3), Path 1, are in a ratio of roughly 3 to 1. As the temperature rises, there must be an increasing tendency for the relatively unstable benzoyl radicals to decompose further to yield carbon dioxide and a highly reactive phenyl radical. The extent of this tendency is expressed by the variation of $\frac{C_\infty}{A}$ with temperature.

Both the mechanism suggested by Hey and Waters (17) and that presented lead to the production of free hydrogen radicals. Proof that there is no

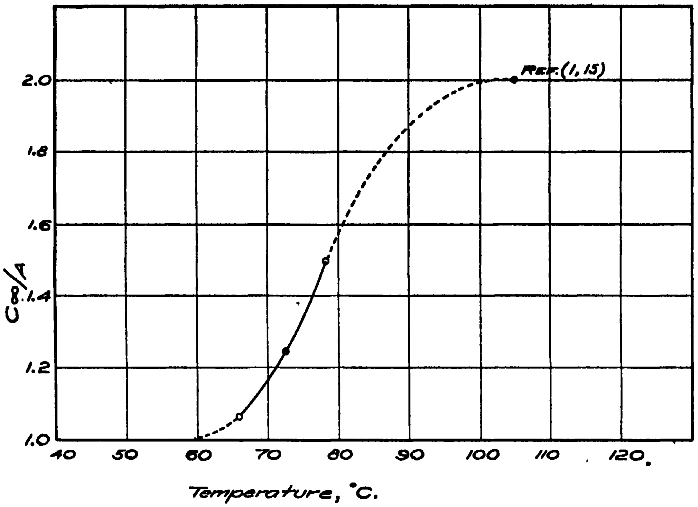


FIG. 1. *Relation between C_∞/A and temperature. Dotted portions of the line are assumed.*

appreciable union of these to form molecular hydrogen as suggested in Equation (iv, *b*) was obtained by the gravimetric determination of evolved carbon dioxide. The values of C_∞/A calculated from these determinations are given in Table V and are in substantial agreement with those obtained from volume measurements (Table I). Were hydrogen produced, the gravimetric values would certainly be lower. Elsewhere (26) it has been shown that phenyl radicals do not combine in solution to give diphenyl. On the basis of this evidence, Reactions (iv *b*, *c*) must occur only rarely if at all. It seems highly probable therefore, that a reaction between the aforesaid radicals (iv*a*) must take place with particular ease. The presence of comparatively large amounts of residue containing oxygen may be explained if it is assumed that the phenyl radicals react with the ester and acid radicals.

References

1. BÖESEKEN, J. and HERMANS, P. H. Ann. 519 : 133-139. 1935.
2. BRODIE, B. C. Ann. 129 : 282-286. 1864.
3. BRODIE, B. C. Ann. Suppl. 3 : 200-226. 1864–1865.
4. BROWN, D. J. J. Am. Chem. Soc. 62(10) : 2657-2659. 1940.
5. CONANT, J. B. and KIRNER, W. R. J. Am. Chem. Soc. 46(1) : 232-252. 1924.
6. FICHTER, F. and FRITSCH, A. Helv. Chim. Acta, 6 : 329-336. 1923.
7. GATTERMANN, L. Laboratory methods of organic chemistry. Revised by H. Wieland. The Macmillan Company, New York and London. 1932.
8. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 285-294. 1925.
9. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 476-479. 1925.
10. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 479-481. 1925.
11. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 764-765. 1925.
12. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 765-770. 1925.
13. GELISSEN, H. and HERMANS, P. H. Ber. 58 : 770-772. 1925.

14. Gelissen, H. and Hermans, P. H. Ber. 59 : 63-68. 1926.
15. Gelissen, H. and Hermans, P. H. Ber. 59 : 662-666. 1926.
16. Hey, D. H. J. Chem. Soc. 1934 : 1966-1969. 1934.
17. Hey, D. H. and Waters, W. A. Chem. Revs. 21(1) : 169-208. 1937.
18. Kamenskaja, S. and Medwedew, S. Acta Physicochim. U.R.S.S. 13 : 565-586. 1940.
19. Lippmann, E. See Reference (8).
20. Moelwyn-Hughes, E. A. Kinetics of reactions in solution. The Clarendon Press, Oxford. 1933.
21. Orndorff, W. R. and White, J. Am. Chem. J. 15(5) : 347-356. 1893.
22. Reynhart, A. F. A. Rec. trav. chim. 46 : 68-71. 1927.
23. Rice, F. O. and Rice, K. The aliphatic free radicals. Johns Hopkins Press, Baltimore. 1935.
24. Walker, O. J. and Wild, G. L. E. J. Chem. Soc. 1937 : 1132-1136. 1937.
25. Waters, W. A. Trans. Faraday Soc. 37 : 770-781. 1941.
26. Wieland, H., Popper, E., and Seefried, H. Ber. 55 : 1816-1834. 1922.
27. Wieland, H., Schapiro, S., and Metzger, H. Ann. 513 : 93-106. 1934.

THE SAP OF THE BIRCH TREE, *BETULA PAPYRIFERA* MARSH.

I. THE AMYLASE SYSTEM[1]

BY E. BOIS[2] AND W. O. CHUBB[3]

Abstract

The amylase system of birch sap consists of a cellobiogenic amylase and most probably a glucogenic amylase. The optimum conditions of pH and temperature are pH 5.5 at 4° C. to 6.3 at 60° C. The maximum production of cellobiose occurred at a temperature of 50° C. at the optimum pH for this temperature. The optimum conditions for the production of glucose were pH 5.5 and a temperature of 50° C.

It is felt that these new facts throw some additional light on the constitution of starch, and that possibly birch sap might serve as a source of cellobiose, which has heretofore only been prepared commercially by hydrolysis of cellulose acetate.

Introduction

In 1833 Payen isolated a concentrate of barley diastase and recognized it as belonging to a new class of substances now called enzymes. Since then a large number of papers have been published concerning this and other amylases.* However, very few dealt with the possibility of the production, by amylases, of sugars other than maltose, the presence or kinetics of the amylases chiefly being investigated. Among the few are notably those by Bailey (2), Bois and Chubb (3), Bois and Nadeau (4), Brown and Millar (7)†, Falk and McGuire (9), Gottschalk (11), Gray (12), Ling (8, 16, 17)‡, Pringsheim and Leibowitz (21), Sjöberg (22), Tallarico (25), Vinson (26), Wrede (20, p. 257; 28), Wülfert (29).

It was decided to investigate the sap of a tree, since, on the assumption that conditions would parallel those in the sugar maple sap, it was likely to be a ready aqueous solution of any amylases present (5). The white birch was chosen because its sap runs very plentifully in the spring.

Experimental

In preliminary tests, mixtures were made up of 1% soluble starch solution and fresh birch sap in the presence of toluene. The mixtures were buffered at various pH values, allowed to react at different temperatures, and the speed of hydrolysis of the starch was followed by means of the iodine–starch coloration. It was found that the variations in the rate of hydrolysis of the

---

[1] *Manuscript received March 2, 1942.*

Contribution from the Biochemistry Laboratory, Faculty of Science, Laval University, Quebec, Que.

[2] *Professor of Biochemistry.*

[3] *Holder of a Bursary under the National Research Council of Canada, 1937-38; Quebec Provincial Bureau of Scientific Research, 1938-39, 1939-40, first half of 1940-41. At present, Chemist, St. Lawrence Sea Products Company, Quebec, Que.*

* *See Walton (27) for a comprehensive bibliography up to 1925.*

† *See also Walton (27), Abstract No. 288.*

‡ *See Walton (27), Abstracts Nos. 307, 312, 314.*

starch, caused by varying the pH and temperature of the samples, were reproducible. Mixtures in which a boiled sap was used exhibited no hydrolysis at the end of two weeks, nor did mixtures containing sap that had been heated to 80° C. for 15 min.

It was concluded therefore that the sap contains an amylase system which is completely inactivated on being heated to 80° C. for 15 min.

Products of the Hydrolysis of Starch by Birch Sap

It was found that two reducing sugars in the sap reacted with the phenylhydrazine reagent to give glucosazone and cellobiosazone. The osazones were identified by means of their melting points and mixed melting points (using osazones prepared directly from the pure sugars). With a set of standard thermometers, the melting points obtained by means of the capillary tube method were 201° C. for the glucosazone and 194° to 197° C. for the cellobiosazone. The reducing sugar that gave glucosazone did not react with Seliwanoff's reagent and was therefore not fructose or invert sugar (ketose), nor did it react in the cold with the phenylhydrazine reagent (mannose). It was therefore concluded that it is glucose.

The absence of sucrose was verified by means of a test with invertase.

To ascertain what sugars were produced in the hydrolysis of starch by the sap *in vitro* a mixture was made of dialysed sap and starch solution and phosphate buffer solution to buffer the whole at a pH of about 6.0. (Toluene was added to this, as to all subsequent digestion mixtures, as preservative.) The crystal forms of the osazones obtained from the sugars produced were the same as those from the sugars in the sap.

Properties of the Birch Sap Amylolytic System

The amylolytic activity of the sap was estimated at different temperatures and pH values by determining the amount of total reducing sugars (calculated as dextrose) produced in 24 and 48 hr.

The digestion samples were at first made up of a mixture of 4 parts sap, 4 parts 1% soluble starch solution, 1 part phosphate buffer solution and, of course, an excess of toluene; later the proportions were changed to 5 : 5 : 1. Blanks in which water replaced the starch solution were run with each determination and, at first, second blanks containing water instead of sap were also used but they were found to be unnecessary. For any one series of determinations, at different pH values and temperatures, homogeneous portions of sap and starch solution were used throughout.

The amounts of reducing sugars were determined in a 5 ml. sample using the Luff-Schoorl method (6, p. 830; 18) and, as noted above, calculated as milligrams dextrose increase.

The pH values of the samples were in all cases measured (using a glass electrode) after, and in some before, the digestion period.

It must be noted in this connection that some trouble was encountered in the buffering of the digestion mixtures. During the 48 hr. reaction period the pH was found to vary considerably, in some cases as much as 0.3 pH units. It was ascertained that these variations were partly due to the soft glass of the containers, and it is probable that some part was due to the loss of free carbon dioxide (which was contained in the sap). But other, unknown, factors also probably contribute to the variation.

The temperatures were constant to about ± 0.25° C. except the temperature of 23° (that of the room) which varied not more than about 2°.

In this manner the amylolytic activity of the sap was estimated at pH values of 4.8, 5.5, 6.1, and 7.3 at temperatures of 6°, 23°, 50°, and 60° C.

The results of these determinations (expressed as increase in reducing sugars as a function of the pH at each temperature) gave curves of the same form (see Fig. 1). It can be seen from these curves that the optimum pH, at all temperatures, was about 5.5. And, at this pH, the optimum temperature was about 50° C. Also, as would be expected, at the extremes of pH the activity was greatly diminished at the higher temperatures. At a pH of 7.3 and at 50° C. the sap was inactivated in less than 24 hr.

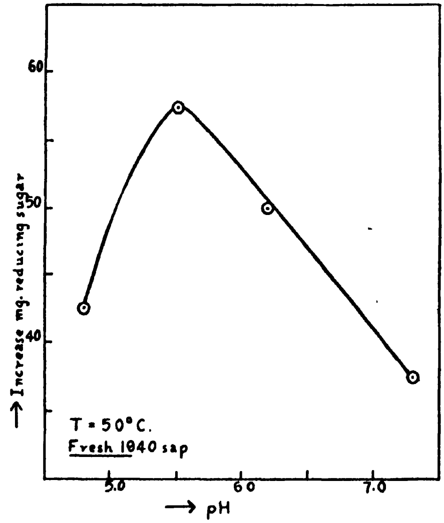


FIG. 1. *Amylolytic activity of sap.*

For a more complete investigation of the amylase system in the sap, it was necessary to estimate the production of glucose and cellobiose separately. Since both are reducing sugars it would be necessary to separate them, eliminate one or hydrolyse the cellobiose. An attempt at hydrolysis was first made but it was found that the necessary conditions would cause at least a partial hydrolysis of the dextrins formed during the starch degradation. After 17 hr. at 70° C., using the acid mixture standard for the cold inversion of sucrose (1, p. 473, sec. XXXXIV, par. 23 (*c*)), cellobiose was only approximately 50% hydrolysed.

As it was reported by Skraup and König (23, 24) that cellobiose is not fermented by brewer's yeast, it was decided to try a method based on the elimination of the glucose in the mixture of sugars by alcoholic fermentation, leaving cellobiose as a residue that could be determined in the usual manner. A method that was satisfactory for the writers' purposes was worked out.

It consisted in pasteurization of the sample, after adjustment of the pH, addition of Fleischman's yeast, allowing to stand overnight at 37° C., addition of defecant (alumina cream), making to volume, filtering, and determining the cellobiose in an aliquot of the filtrate.

Using this method it was found that the rate of production of cellobiose, during the hydrolysis of starch in contact with the sap for 48 hr., varied with the pH and temperature of the mixture. This indicated the presence of a cellobiogenic amylase.

The rates of production of glucose and cellobiose by hydrolysis of starch by the sap were determined at various temperatures and pH values (reaction time, 48 hr.). Two series of determinations were made, one using a sap from the 1939 run, one year old, and the other using a fresh sap from the 1940 run.

In general form the activity curves were similar, as were also the optimum pH values and temperatures (see Figs. 2 and 3). For the production of glucose the optimum pH was 5.5 and, at this pH, a temperature of 50° C. For the production of cellobiose the optimum pH varied from 5.5 at 4° and 23° to 6.3 at 60° C. The variation between 23° and 37° C. was the greatest, being from 5.5 to 6.0. The greatest production of cellobiose occurred at 50° C., as in the case of glucose.

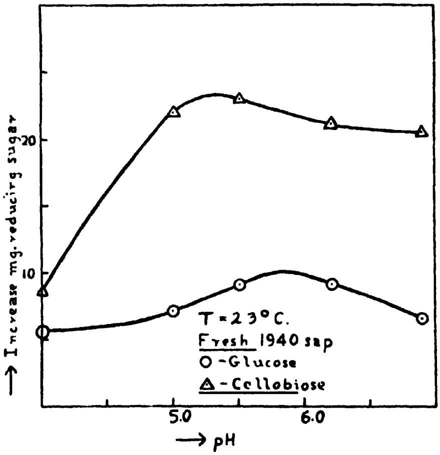


FIG. 2. *Production of sugars at 23°C.*

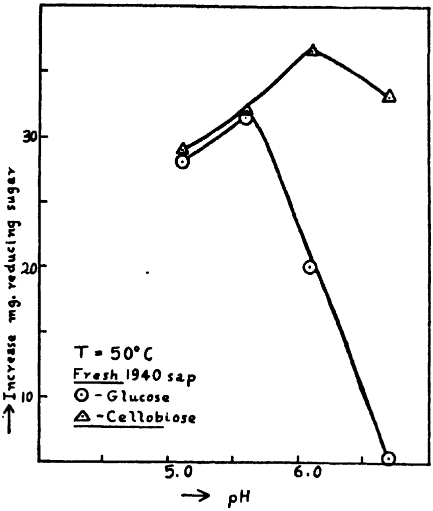


FIG. 3. *Production of sugars at 50°C.*

If the temperature-activity curves, at constant pH, are plotted (using the above data) it can be seen that the rates of production of both sugars fall off sharply once the optimum temperature, at each pH, has been passed. The curves show that at the higher pH values the cellobiogenic amylase is more resistant to inactivation by heat than the glucogenic amylase. At a pH of 6.8 the activity of the glucogenic amylase decreases at temperatures higher than 37° C. But at lower pH values, for example at 5.1, the activity of the cellobiogenic amylase decreases, after the optimum temperature for this pH has been reached, much faster than that of the glucogenic amylase.

The activities of the sap at pH 6.0 and 37° C. were determined from day to day during the entire 1940 run. There were no significant variations.

Oligosaccharases

It was thought possible that the glucose produced during the hydrolysis of starch, in contact with the sap, might have been due to an enzymatic hydrolysis of some of the cellobiose; therefore, tests were carried out to show the presence or absence of cellobiase. Fresh saps of the 1939 and 1940 runs were used. The test was carried out by supplying a substrate of cellobiose to the sap and determining the reducing power of the mixture before and after 48 hr. at 37° C. There was no increase in reducing power; consequently, cellobiase was absent.

Similar tests, using sucrose as substrate, were carried out, and these demonstrated the absence of invertase in the same saps.

Discussion

It has been shown above that the sap contains only two reducing sugars, glucose and cellobiose, and also that these are the sugars produced by the degradation of starch by the sap *in vitro*. It was concluded therefore that there is in the sap at least a cellobiogenic amylase.

But it might be expected that the glucose would be produced from the cellobiose, or perhaps from some other oligosaccharide, by enzymatic hydrolysis. It has been shown that the sap contains no cellobiase, so the glucose is not produced from the cellobiose. And since it has also been shown that there is no invertase in the sap, the glucose could not be produced from sucrose. The only other non-reducing disaccharides known that yield glucose only on hydrolysis are trehalose and isotrehalose. These sugars have, to date, been found in fungi only, where they are widely distributed. At the time it was not possible to investigate the possibility of the production of glucose from starch by means of a phosphorylase (see Hanes (13, 14)). Such an investigation is projected in this laboratory for the near future. In the meanwhile it is tentatively concluded that the glucose may be produced directly from starch by a glucogenic amylase.

One of the most widely accepted theories of the constitution of starch today envisages the molecule as made up of a large number of glucopyranose units joined into chains by maltose or α-linkages exclusively, these chains being joined together by some side linkages probably due to residual valencies. Haworth (15), who subscribes to this theory, bases his belief on (*a*) the fact that common diastases give only maltose and glucose by the hydrolysis of starch, and also on (*b*) the results of some acetolyzing experiments on a methylated starch. In the same way he claims to have proved that cellulose is made up of cellobiose units or alternating α- and β-linkages between the glucopyranose foundation units. Thus, maltose and cellobiose are regarded as the characteristic products of hydrolysis of starch and cellulose respectively.

Freudenberg (10) holds similar but slightly modified views. He considers the starch molecule as made up almost wholly of maltose units with only one other type of bond to every 20 or 25 maltose units. However, he is of the opinion that the maltose units are connected not in straight chains but in branched chains or branched rings. He advances as proof the results of some methylation experiments.

Myrbäck (19) favours the maltose linkage theory but emphasizes that any theory of the constitution of starch must account not only for its chemical behaviour but also, and in a satisfactory manner, for the action of the starch hydrolyzing enzymes.

It has been shown by the authors that cellobiose is produced by starch hydrolysis, and it has been shown by Bois and Nadeau (4) that both this sugar and sucrose are so produced. The claim is advanced therefore that any theory of the constitution of starch must not only account for the production of cellobiose, which differs from maltose only by the type of linkage between the two glucopyranose units, but also for the production of sucrose, which differs fundamentally from maltose in structure, containing a fructo-furanose ring connected to a glucopyranose ring.

Moreover Freudenberg's modification cannot account for the production of these sugars, since a maximum of one in twenty, or 5% only, of sugars other than maltose can, according to his theory, be produced. And the authors have shown, as have Bois and Nadeau (5), that much greater yields of cellobiose and sucrose can be produced. For example, a yield of cellobiose, at 50° C. and a pH of 6.1, was obtained which was equivalent to a starch hydrolysis of about 33.3%. Bois and Nadeau obtained a yield of cellobiose, at 50° C. and a pH of 6.6, equivalent to a 45.4% hydrolysis, and a yield of sucrose, at 8° C. and a pH of 6.6, equivalent to a 40% hydrolysis.

It is submitted by the authors that these facts should be explained by a true theory of the constitution of starch.

References

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis. 4th ed. A.O.A.C., Washington, D.C. 1935.
2. Bailey, E. M. J. Am. Chem. Soc. 34 (12) : 1706-1730. 1912.
3. Bois, E. and Chubb, W. O. Can. Chem. Process Ind. 22 : 322. 1938.
4. Bois, E. and Nadeau, A. Can. J. Research, B, 16 (4) : 114-120. 1938.
5. Bois, E. and Nadeau, A. Can. J. Research, B, 16 (4) : 121-133. 1938.
6. Brown, C. A. and Zerban, F. W. Sugar analysis. New York. 1941.
7. Brown, H. T. and Millar, J. H. J. Chem. Soc. 75 : 315-337. 1899.
8. Davis, B. F. and Ling, A. R. J. Chem. Soc. 85 : 16-29. 1904.
9. Falk, K. G. and McGuire, G. J. Gen. Physiol. 3 (5) : 595-609. 1921.
10. Freudenberg, K. Ann. Rev. Biochem. 8 : 81-107. 1939.
11. Gottschalk, A. Z. physiol. Chem. 152 : 132-135. 1926.
12. Gray, P. H. H. Can. J. Research, C, 17 (5) : 154-169. 1939.
13. Hanes, C. S. Proc. Roy. Soc. (London) B, 128 : 421-450. 1940.
14. Hanes, C. S. Proc. Roy. Soc. (London) B, 129 : 174-208. 1940.
15. Haworth, W. N. Chemistry & Industry, 58 (41) : 917-925. 1939.
16. Ling, A. R. J. Inst. Brewing, 9 : 446-461. 1903.
17. Ling, A. R. and Davis, B. F. J. Inst. Brewing, 8 : 475-495; discussion, 495-500. 1902.
18. Luff, G. and Schoorl, N. Rept. Proc. Ninth Session, Intern. Commission for Uniform Methods of Sugar Analysis. 1936.
19. Myrbäck, K. Ann. Rev. Biochem. 8 : 59-80. 1939.
20. Pringsheim, H. Chemistry of the saccharides. McGraw-Hill Book Company, Inc., New York and London. 1932.
21. Pringsheim, H. and Leibowitz, J. Ber. 58 : 1262-1265. 1925.
22. Sjöberg, K. Z. physiol. Chem. 162 : 223-237. 1927.
23. Skraup, Z. H. and König, J. Ber. 34 : 1115-1118. 1901.
24. Skraup, Z. H. and König, J. Monatsh. 22 : 1011-1036. 1901.
25. Tallarico, G. Arch. farmacol. sper. 7 : 27-48, 49-68. 1908.
26. Vinson, A. E. Botan. Gaz. 43 : 392-407. 1907.
27. Walton, R. P. A comprehensive survey of starch chemistry. Vol. 1. The Chemical Catalog, Inc., New York. 1928.
28. Wrede, H. Papier-Fabr. 27 (13) : 197-202. 1929.
29. Wülfert, K. Biochem. Z. 302 : 232-246. 1939.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. JULY, 1942 NUMBER 7

THE HYDROLYSIS OF PROPIONITRILE IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS[1]

BY B. S. RABINOVITCH[2], C. A. WINKLER[3], AND A. R. P. STEWART[4]

Abstract

The hydrolysis of propionitrile has been studied in aqueous hydrochloric acid solutions from 0.5 to 10 N and over a range of temperatures at six acid concentrations. The rate of hydrolysis as measured by ammonia formation is dependent upon the decomposition of the intermediate amide at acid concentrations above 4 N. The system represented by nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid affords a good example of consecutive, irreversible unimolecular reactions over the complete range $k_1 \ll k_2$ (below 4 N) to $k_1 \gg k_2$ (above 11 N). A marked increase in rate with increasing acid concentration is accounted for in large measure by a decrease in observed activation energy of 6.7 Cal. over the range 1 to 10 N.

Introduction

A recent communication (19) from this laboratory on the hydrolysis of amides in concentrated hydrochloric acid solutions has emphasized the importance of determining the parameters of the Arrhenius equation over the entire range of acid concentrations used. It seemed of particular interest to extend the investigation of the Arrhenius constants for reactions in concentrated acid solutions to the hydrolysis of aliphatic nitriles. This reaction has rate characteristics which differ from those for amide hydrolysis. The rate of nitrile hydrolysis increases more rapidly with increase of acid concentration than any other reaction studied in concentrated acid solution (11), whereas that of amide hydrolysis, as measured by the unimolecular constants, passes through a maximum value at around 3 to 6 N acid (10). Furthermore, relatively few data on activation energies for nitrile hydrolysis are available.

The hydrolysis of nitriles proceeds through the amide to yield ammonia and the corresponding acid, according to the equation:

$$RCN \xrightarrow{H_2O} RCONH_2 \xrightarrow{H_2O} RCOOH + NH_3$$

The rate of reaction for simple aliphatic nitriles is generally regarded as being much slower than the rate of amide hydrolysis. In a recent paper, Krieble and Noll (11) have assumed that this rate relation is maintained up to hydro-

---

[1] *Manuscript received in original form February 4, 1942, and as revised, April 25, 1942.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Postgraduate student, McGill University, and holder of a Studentship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry.*

[4] *Student at the University of Manitoba, Winnipeg, Man.*

chloric acid concentrations of the order 8 to 14 molal. They suggest that at still higher concentrations the rate of reaction, as measured by ammonia production, may no longer be independent of the hydrolysis of the intermediate amide. However, in view of the different way in which the rates of the two reactions are influenced by acid concentration, it appeared that the rate of nitrile hydrolysis should be comparable with that of amide hydrolysis at concentrations below the maximum used by Krieble and Noll. This supposition was supported by comparison of the rate data for amides obtained in the previous study (19) with their values for nitriles.

Since there was some uncertainty about the part played by hydrolysis of the intermediate amide in nitrile hydrolysis, it was obviously necessary to clarify this point before investigating the Arrhenius equation for a number of nitriles. This question has therefore been investigated during a study of the Arrhenius constants for the hydrolysis of propionitrile by hydrochloric acid, over a range of concentrations from 0.5 to 10 *N*.

Materials and Procedure

Propionitrile was obtained commercially and was purified to a boiling range of 0.2° C. on a column of the Whitmore type. Aqueous solutions of the nitrile were made by weight to give a concentration in the reaction mixtures of approximately 0.2 *N*.

Acid solutions were prepared by dilution of reagent grade, concentrated hydrochloric acid, previously standardized by density measurements and titration.

At acid concentrations other than 10 *N*, reaction mixtures of desired composition were prepared by mixing appropriate volumes of nitrile and acid solutions at 0° C. Concentrations after mixing were calculated from the density–percentage data for hydrochloric acid in International Critical Tables. Since the nitrile solutions were dilute, they were treated as pure water in these calculations. Small Pyrex tubes, filled so as to leave little dead space, were sealed and immersed in thermostats regulated to within 0.1° C. Temperature was measured with standard thermometers. An experimentally determined correction was applied for the time required for the solutions to come to reaction temperature. The duration of even the shortest runs exceeded an hour. At acid concentration of 10 *N*, where the reaction temperatures were lower, the solutions were brought to temperature prior to mixing in a stoppered, glass reaction vessel.

The rate of production of ammonia alone was followed by Folin's aspiration method (3), calibrated and applied at 0° C. in a standard manner. Experiments with standard propionamide solutions showed that a constant fraction of 2% of the amide present was converted to ammonia during analysis. No correction was considered necessary for the present purposes. Blank experiments showed no hydrolysis of nitrile under these conditions.

Total amide and ammonia were determined by a modified technique. The alkaline solution was aspirated for 10 min. at 0° C. and while being heated to 90° C., during which time all nitrile was removed. The solution was then held at 90° C. without aspiration for three-quarters of an hour, after which air was again passed through to remove ammonia formed by hydrolysis of the amide. Experiments with propionamide solutions showed that all the amide was hydrolyzed to ammonia under these conditions.

Results

In Table I are recorded typical unimolecular constants for experiments at various temperatures in which the rate of reaction was measured by determination of both ammonia and amide, and of ammonia alone. When the data for ammonia production alone are considered, it is evident that at acid concentrations up to and including 4 *N* there is no indication that rate of ammonia production fails to measure rate of nitrile hydrolysis. At 5 *N*, however, a small induction period is evident; it becomes very prominent at 6.5 and 8.5 *N*, although the *k* values tend to level off in the later stages of the reaction. With 10 *N* acid, the induction period again becomes relatively small.

TABLE I

NATURE OF THE INDUCTION PERIOD IN THE HYDROLYSIS OF PROPIONITRILE AT DIFFERENT CONCENTRATIONS OF HYDROCHLORIC ACID

Concentration of hydrochloric acid, normality	Temp., °C.	Analytical method: A—ammonia AA—ammonia + amide	$k \times 10^2$ hr.$^{-1}$						
			Per cent NH_3*						
			10 – 20	20 – 30	30 – 40	40 – 50	50 – 60	60 – 70	70 – 80
1.00	59.6	A	0.0585 0.0589	0.0582 0.0579					
2.00	59.6	AA	0.152	0.147	0.152	0.154	0.149		
4.00	99.7	A	39.2	40.0		39.7	40.1	39.0	
	99.7	AA	39.7	38.8	39.1	39.8	38.8		
5.02	83.1	A	18.7		20.7	20.4	20.8	20.0 20.4	
	49.6	AA	0.574	0.569	0.584	0.582	0.573	0.586	
6.48	50.1	A	2.00			3.42	3.55	3.56 3.62	
	49.9	AA	3.53	3.51	3.52	3.51	3.48		
8.47	59.6	A	16.9		23.6 26.2	32.6	32.7	34.6	32.8
	59.6	AA	122	122	122	117	123	121	
10.13	40.2	A	29.6	30.9		32.0	32.2 31.5	31.8	
	24.7	AA	31.2	30.8	29.1	31.6	29.7	31.4	29.0

* *Refers to percentage ammonia for runs analysed for ammonia; given to indicate the region in which k values were determined.*

When total amide and ammonia is measured, the induction period is absent at all acid concentrations. In the concentration range above 4 *N*, therefore, the rate of amide hydrolysis influences the rate of the over-all reaction and in this range the true rate of nitrile hydrolysis is given by determination of total amide and ammonia, and not of ammonia alone.

The first order velocity constants obtained over a temperature range at each of several acid concentrations are recorded in Table II. Each value of *k* is the mean of five or six determinations, total amide and ammonia being measured in every instance. The average deviation of the observed *k* values from the recorded mean was usually about 1% for concentrations below 5 *N*,

TABLE II

UNIMOLECULAR VELOCITY CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE WITH HYDROCHLORIC ACID

Concentration of hydrochloric acid, normality	Concentration of nitrile, normality	Temperature, °C.	$k \times 10^2$ hr.$^{-1}$
0.509*	0.2002	59.6	0.0259
1.00*	0.2002	59.6	0.0584
		83.4	0.762
		93.3	2.03
		99.6	3.92
		111.8	11.1
2.00	0.2002	59.6	0.151
4.00	0.2004	49.6	0.222
		59.6	0.672
		79.7	5.71
		94.0	24.5
		99.7	39.2
4.55	0.2004	59.6	1.18
5.02	0.2239	50.8	0.694
		59.6	1.74
		70.6	5.41
		83.1	20.4
6.48	0.1995	38.3	0.991
		49.9	3.51
		59.6	10.0
		72.6	32.4
8.47	0.1734	30.7	7.19
		38.3	15.6
		59.6	122
10.13	0.1770	0.0	1.67
		16.8	12.1
		24.7	30.4
		34.5	80.2

* *At these lower concentrations, a downward drift in velocity due to depletion of the catalyst by ammonia formation was observed and taken into account.*

and 1 to 2% for other concentrations. All concentrations were taken without correction as at 25° C., and no correction has been applied for variation of collision number with temperature. These errors partially cancel and should be negligible for comparative purposes.

The constants of the Arrhenius equation, $k = Ae^{-E/RT}$, calculated from the data at each acid concentration, are shown in Table III. The relation was satisfactorily obeyed in all cases. To obtain A, the velocity constants were expressed in seconds, and divided by the normality of the solutions to reduce all data to unit acid concentration. Although correct in principle, this procedure is arbitrary as the proper function of acid concentration, in terms of which velocities should be expressed, is not known. This difficulty is common to this and many other investigations of concentrated acid catalysis. Errors in the E values, as determined by consideration of the poorest and best Arrhenius lines, do not exceed 100 to 200 cal. at acid concentrations of 1, 4, and 6.5 N, and 300 to 400 cal. at other concentrations. The probable errors are less than these values.

TABLE III

THE ARRHENIUS CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE AT VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID

Concentration of hydrochloric acid, normality	$\log_{10} A$	E, cal.
1.00	10.04	25,600
4.00	9.95	24,800
5.02	9.68	23,900
6.48	8.92	21,800
8.47	8.85	20,100
10.13	8.78	18,900

At hydrochloric acid concentration of approximately 0.5 N, Kilpi (8) has found an activation energy of 25,800 cal. for the hydrolysis of propionitrile

TABLE IV

DATA ILLUSTRATING THE INCREASE OF RATE OF PROPIONITRILE HYDROLYSIS WITH INCREASE OF HYDROCHLORIC ACID CONCENTRATION (59.6° C.)

Concentration of hydrochloric acid, normality	0.509	1.00	2.00	4.00	4.55	5.02	6.48	8.47	10.13
$k \times 10^2$ hr.$^{-1}$	0.0259	0.0584	0.151	0.672	1.18	1.74	10.0	122	830*

* *Obtained by extrapolation of the Arrhenius line.*

in alcohol–water medium. No other data are available with which to make comparison.

Parallelism in changes of A and E, similar to that exhibited in this study, has been frequently observed and has been interpreted by several investigators.

The great sensitivity of the reaction rate to acid concentration is well illustrated in Table IV. A 20-fold increase in acid concentration results in an increase in rate by a factor of approximately 3×10^4, with no evidence that a maximum rate is attained at higher concentrations, as has been suggested (11).

A few experiments made with sodium chloride present in the reaction solution showed a positive primary neutral salt effect which increased with acid concentration (Table V). A similar behaviour for hydrocyanic acid has been pointed out before (12).

TABLE V

DATA ILLUSTRATING NEUTRAL SALT EFFECT IN THE HYDROLYSIS OF PROPIONITRILE BY HYDROCHLORIC ACID

Hydrochloric acid concentration, normality	Sodium chloride concentration, normality	$k_{49.6^\circ C.} \times 10^2$ hr.$^{-1}$
2.00	—	0.151
	1.9	0.217
4.00	—	0.672
	0.99	0.938

Discussion

The investigation of the system, propionitrile $\xrightarrow{k_1}$ propionamide $\xrightarrow{k_2}$ propionic acid + ammonia, has revealed the interesting fact that it provides an example of consecutive, irreversible unimolecular reactions over the complete range $k_1 \ll k_2$ (below 4 N) to $k_1 \gg k_2$ (estimated above 11 N). The characteristics of such systems, which constitute the simplest type of successive reactions, have been known for many years, and the existing treatments of the problem in general, and for nitriles and amides in particular (8), are adequate. A detailed discussion of this aspect of the present study would therefore seem unnecessary.

The nature of the nitrile–amide rate relations derive from the fact that, while the rate of amide hydrolysis increases to a maximum value at hydrochloric acid concentration of about 3 N and then decreases (10), the rate of nitrile hydrolysis increases rapidly and continuously with increase of acid concentration, especially at higher concentrations (Table IV). The relative rates of the two reactions at 49.6° C., for the concentration range 1.00 to 10.13 N, are recorded in Table VI. Most of the values have been taken directly from experimental data or the Arrhenius lines; others were computed as indicated.

TABLE VI

DATA ON THE RELATIVE RATES OF HYDROLYSIS OF PROPIONITRILE AND PROPIONAMIDE

Hydrochloric acid concentration, normality	$k_{49.6°C.} \times 10^2$ hr.$^{-1}$			
	Propionamide (19)	Propionitrile (analysed for NH_3 only)	Propionitrile (analysed for total amide +ammonia)	Ratio amide : nitrile*
1.00	39.1	0.0174		2000 : 1
4.00	71.1	0.222	0.219	300 : 1
5.02	54‡	0.573	0.578	90 : 1
6.48	33.9	3.71**	3.42	10 : 1
8.47	15.3	13.2†	47.9	1 : 3
10.13	8.62	8.48	350	1 : 40

* *Given in round figures; the ratio varies with temperature.*

† *Obtained by extrapolation of the k–% reaction curve to 100%.*

‡ *Obtained by interpolation of values at neighbouring concentrations.*

** *This value refers to 50.1° C.*

Adapting Mellor's calculation for consecutive, irreversible, unimolecular reactions (17, p. 118), a slight induction period in the rate of the slowest reaction, as determined by analysis of the final product (in this case ammonia) should be evident when the ratio of the velocity constants is of the order 100 : 1. This corresponds in the present study to acid concentrations of 5 *N*, where k_2, the amide constant, is the larger, and to 10 *N* acid, where k_1, the nitrile constant, is the larger, in agreement with the observed behaviour (Table I). The calculations further show that for a ratio of the rate constants of about 10 : 1, a marked induction period should occur, while for smaller values of the ratio the measured velocity of the slowest reaction does not attain its true value. This corresponds to the behaviour found for 6.48 *N*, where the measured rate eventually equals that of the nitrile, and for 8.47 *N* where the rate approaches that for the amide (Tables I and VI).

The time curves obtained experimentally at each acid concentration for the amount of nitrile hydrolysed, the amount of ammonia formed, and the concentration of the intermediate amide, each expressed as a percentage of the original concentration of nitrile, are characteristic. In Fig. 1*a* are shown the curves for 6.48 *N* acid, characteristic of the type $k_1 < k_2$, while in Fig. 1*b* are shown those for 8.47 *N* acid, of the type $k_1 > k_2$. The dotted lines for intermediate amide concentration have been calculated independently from the well known equation,

$$[\text{amide}] = \frac{ak_1}{k_2 - k_1}\left(e^{-k_1t} - e^{-k_2t}\right),$$

where *a* is the initial concentration of nitrile. The values of k_2 obtained in the previous study were used. The agreement between observed results

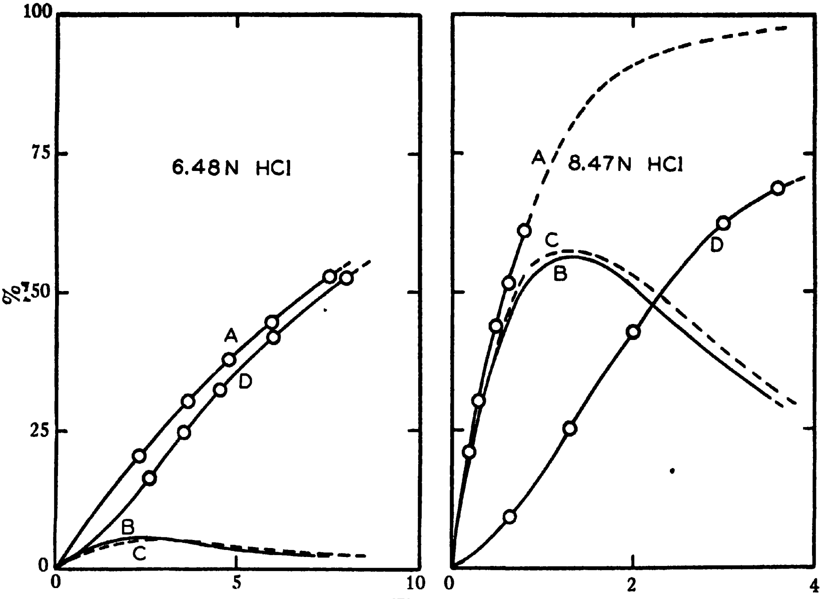


Fig. 1*a*

Fig. 1*b*

FIG. 1. *Curves showing the nature of the consecutive reactions of propionitrile and propionamide at hydrochloric acid concentrations of (a) 6.48 and (b) 8.47 N. A, nitrile hydrolysed; B, amide concentration found; C, amide concentration caculated; D, ammonia produced.*

and those calculated on the basis of the analysis of the system presented here is quite satisfactory.

In view of the behaviour revealed by the present study, earlier results (11) obtained for the hydrolysis of propionitrile in concentrated hydrochloric acid solutions contain error since no account was taken of the part played by amide hydrolysis in determining the rate of the over-all reaction. Actually, the rate measured at 14.9 molal in that investigation corresponds approximately to the rate of amide hydrolysis at this concentration.

An outstanding characteristic of the propionitrile hydrolysis is the rapid increase in rate with acid concentration demonstrated by the data in Table IV. The hydrolysis of other nitriles is analogous to that of propionitrile in this respect. Krieble and co-workers (11, 12) have related the rapid rate increase to the square of the mean ion activity and, on that basis, have suggested that hydrochloric acid molecules are the principal catalyst. However, for nitriles other than hydrocyanic acid there is considerable variation in the ratio $k/a_{\pm}^{2}$ over the range of acid concentrations. The lack of constancy is apparently not due simply to the fact that their data at higher acid concentrations do not correspond to the rate of nitrile hydrolysis, as neither $k/a_{\pm}$ nor $k/a_{\pm}^{2}$ have been found to be constant in the present study. The variation of $a_{\pm}^{2}$ parallels the large increase within a factor of about twenty over the entire range of acid concentrations, but other measures of the acid concentration may be adapted to do the same.

The acidity function, H_0, of Hammett (5, p. 267) has been found to be related to the rates of certain acid catalyzed reactions by the expression:

$$H_0 + \log k = \text{constant}.$$

Data for the hydrolysis of cyanamide in nitric acid solutions of concentrations up to 5 N (4) exhibit the theoretical linear relation of unit slope. Using values of H_0 obtained by interpolation or extrapolation of the data of Hammett and Paul (6, 7), the data obtained in the present study have been plotted in Fig. 2. It should be recalled that the values of H_0 given by Hammett and Paul refer to indicator solutions in pure acid at temperatures different from those employed here. The graph indicates a linear relation of slope 0.9, for acid concentrations up to 5 N. Deviations from linearity occur at higher concentrations. Reactions which exhibit the relation are, on the basis of the formulation of H_0 by Hammett and the analysis of prototropic reactions given by Pedersen (18), interpreted as being examples of specific hydrogen ion catalysis. The deviations might indicate general acid catalysis. Alternatively, the reaction may be one of specific hydrogen ion catalysis proceeding through an equilibrium cation, since the assumptions on which the Hammett relation is based may not be valid over the wide range of acid concentration concerned here, where large salt and medium effects may be operative (22). This criterion, therefore, leaves the nature of the catalyst in doubt.

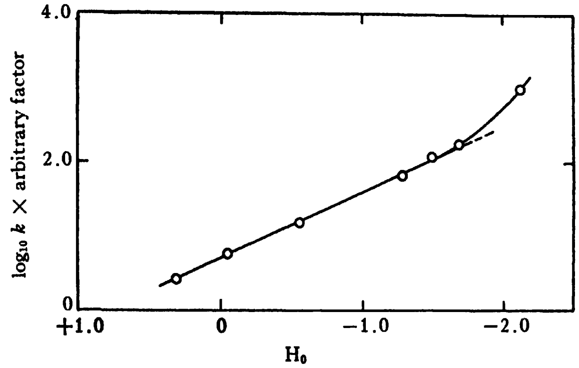


FIG. 2. *Plot of* $\log_{10} k_{99.6°C}$ *against* H_0.

A rapid increase in rate with acid concentration, similar to that observed in the present study, characterizes the cyanamide hydrolysis mentioned previously, and the data have been represented by an empirical relation, formally the same as the familiar one for the primary exponential salt effect. This relation is applicable to propionitrile at concentrations of acid up to 2 to 3 N, but above this concentration the slope increases markedly and continuously with increase of acid concentration. It may be significant that it is in this region that the activation energy begins to undergo marked change. It would obviously be of interest to know whether the Arrhenius constants change over a range of acid concentrations in the hydrolysis of cyanamide, since such changes may occur where the exponential salt effect is obeyed (9, 14). Schmid and Olsen (20) have studied the neutral salt effect for the cyanamide hydrolysis at salt concentrations as high as 2 to 6 N, at a constant nitric acid concentration of 0.25 N. The study was made at two temperatures only, however, and accurate evaluation of E is not possible from their data. Moreover, the increase of rate with salt concentration is not as marked as that observed for increase of acid concentration.

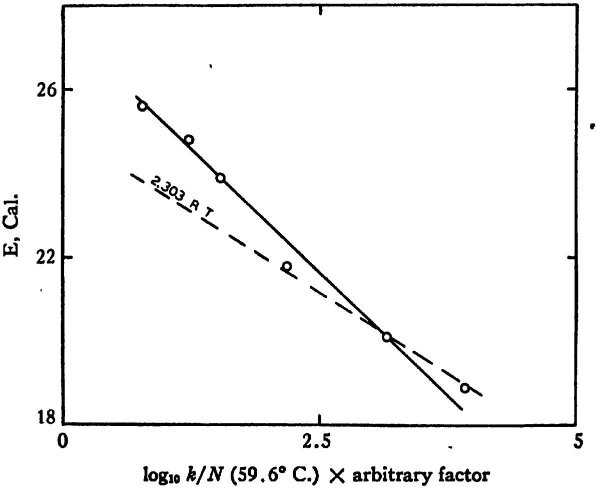


FIG. 3. *Plot of* $\log_{10} k_{59.6°C.}$ *against* E.

Actually, the rapid rate increase with acid concentration shown in Table IV can be accounted for by the observed decrease in activation energy. In Fig. 3 are plotted the values for log k/N against the corresponding activation energies for different acid concentrations. Simultaneous, parallel variation of the A factor may be assumed responsible for deviations from a linear relation of theoretical slope, 2.303 RT, and cause an increase in slope. Its magnitude, however, is of the proper order. At concentrations of 6.48, 8.47, and 10.13 N, where small variation in A occurs, the points lie about a line of theoretical slope.

It seems probable that the observed decrease in activation energy with increased acid concentration represents a fundamental variation. A possible explanation of the decrease, based on the assumption of two catalytic species whose concentrations vary with acid concentration, e.g., oxonium ion and undissociated acid molecules, of which the latter is characterized by a lower activation energy, seems untenable. If this were true, not only would the difference in activation energies have to exceed 6.7 Cal. but there would be sufficient of the more efficient catalyst at all acid concentrations for the reaction to proceed exclusively through its agency.

Another possibility, namely, that a temperature dependence of *E* may cause an apparent variation over the acid concentration range because of the different temperature ranges employed for different acid concentrations, appears to be excluded. The magnitude of the observed shift, the generally small temperature dependence of *E* above 40° C. (14, 15, 16), and the fact that variation in *E* occurs between acid concentrations studied over the same temperature ranges (1 and 4 *N*; 6.5 and 8.5 *N*), are all opposed to such a likelihood.

Dependence of the Arrhenius constants on temperature and variation of this dependence with acid concentration might result in apparent shifts in *E* and *A* (2). Hydrolytic reactions are of the type which display temperature dependence of activation energy (13). Furthermore, in calculating the activation energies, it was not possible to take account of the variation in dielectric constant of the medium with temperature. Reactions of zero ionic type, to which class the hydrolysis of propionitrile belongs, are least sensitive to variations in the dielectric constant (1, 21), although at the high acid concentrations employed here the effect may be uncertain. Also, temperature dependence is usually of decreasing importance in the temperature regions used in the present work, with exception of the experiments at an acid concentration of 10 *N*. No evidence for its existence can be observed from the Arrhenius lines, even in the experiments with 1 and 4 *N* acid, where the most accurate measurements were made and where five temperatures were used over a range of 50° C. It is possible, of course, that the best accuracy attained in the study might be inadequate to detect failure of the Arrhenius equation. Since the temperature variations of *A* and *E* partially compensate, the total possible effect in this eventuality might be expected to be small. Hence, it is believed that, while small temperature dependence of *A* and *E* may possibly have some effect here, the variations of *A* and *E* with concentration are substantially real.

For reactions in which real changes in *A* and *E* occur with variation of catalyst concentration, apparent relations between reaction rate and other factors such as mean ion activity, acidity function, salt effect, etc., probably do not represent fundamental analysis of the factors influencing the reaction.

References

1. Amis, E. S. and Holmes, F. C. J. Am. Chem. Soc. 63 (8) : 2231-2235. 1941.
2. Bell, R. P. Trans. Faraday Soc. 34 : 229-236. 1938.
3. Folin, O. and Farmer, C. J. J. Biol. Chem. 11 : 493-501. 1912.
4. Grube, G. and Schmid, G. Z. physik. Chem. 119 : 19-45. 1926.
5. Hammett, L. P. Physical organic chemistry. McGraw-Hill Book Company, New York and London. 1940.
6. Hammett, L. P. and Paul, M. A. J. Am. Chem. Soc. 56(4) : 827-829. 1934.
7. Hammett, L. P. and Paul, M. A. J. Am. Chem. Soc. 56(4) : 830-832. 1934.

8. Kilpi, S. Z. physik. Chem. 86 : 641-681. 1914.
9. Kiss, A. v. and Bossanyi, I. Rec. trav. chim. 53 : 903-916. 1934.
10. Krieble, V. K. and Holst, K. A. J. Am. Chem. Soc. 60(12) : 2976-2980. 1938.
11. Krieble, V. K. and Noll, C. I. J. Am. Chem. Soc. 61(3) : 560-563. 1939.
12. Krieble, V. K. and Peiker, A. L. J. Am. Chem. Soc. 55(6) : 2326-2331. 1933.
13. La Mer, V. K. and Miller, M. L. J. Am. Chem. Soc. 57(12) : 2674-2680. 1935.
14. Leininger, P. M. and Kilpatrick, M. J. Am. Chem. Soc. 60(12) : 2891-2899. 1938.
15. Leininger, P. M. and Kilpatrick, M. J. Am. Chem. Soc. 61(9) : 2510-2514. 1939.
16. Medvedev, Y. J. Phys. Chem. (U.S.S.R.) 10 : 372-378. 1937.
17. Mellor, J. W. Chemical statics and dynamics. Longmans, Green, and Company, London. 1914.
18. Pedersen, K. J. J. Phys. Chem. 38 : 581-600. 1934.
19. Rabinovitch, B. S. and Winkler, C. A. Can. J. Research, B, 20 (5) : 73-81. 1942.
20. Schmid, G. and Olsen, R. Z. physik. Chem. 124 : 97-114. 1926.
21. Warner, J. C. Ann. New York Acad. Sci. 39(5) : 345-354. 1940.
22. Wynne-Jones, W. F. K. Trans. Faraday Soc. 34 : 245-251. 1938.

THE SYNTHESIS AND THE CHARACTERIZATION OF THE MONOMETHYL- AND THE DIMETHYL-QUINOLINES[1]

By Richard H. F. Manske[2], Léo Marion[2] and Frank Leger[2]

Abstract

All 7 monomethyl- and all 21 dimethyl-quinolines were synthesized by unambiguous methods and those solid above room temperature were purified to their maximum melting points. The picrates, styphnates, and trinitro-*m*-cresolates of each quinoline were prepared and their properties recorded. The picrates in particular were purified to their ultimate melting points. Incidentally, 7-ethyl-quinoline and a number of trimethyl-quinolines were also prepared. It is concluded that the melting points previously given in the literature for most of the picrates are of little use for identification purposes.

Introduction

The preparation of all the monomethyl-quinolines and many of the dimethyl-quinolines has already been recorded. They were prepared by a variety of methods and by many different investigators, and it is not unusual that the recorded properties for the same substance vary by more than reasonable experimental errors. In the course of some degradation experiments with alkaloids, two of the present authors (R.H.F.M. and L.M.) obtained lepidine and 7-methyl-quinoline and found that the melting points of their purified picrates were considerably higher than any values thus far recorded for these well known compounds. Concurrently a dimethyl-quinoline was obtained from the degradation products of another alkaloid. The melting point of its picrate was sufficiently close to the melting points of a number of picrates already described to justify their preparation for purposes of authentication. Here again the recorded values were found to be in serious error, and it was concluded that the literature values for the melting points of the picrates of most of the monomethyl- and dimethyl-quinolines were of little service in identifying such substances. As subsequent events have proved, this conclusion was amply justified.

The 7 monomethyl-quinolines and the 21 dimethyl-quinolines have been prepared by unambiguous syntheses. The 10 quinolines that were solids at room temperature were purified to their maximum melting points, and the picrates, the styphnates, and the trinitro-*m*-cresolates were prepared from all bases after exhaustive purification. The accompanying table is a summary of the melting points of these derivatives. In general the picrates attained their ultimate melting points without further purification, but as a precaution they were all recrystallized at least once. Only when the synthesis produced two substances was it necessary to repeat the recrystallization. The styphnates and the trinitro-*m*-cresolates were not recrystallized except when the

---

[1] *Manuscript received March 26, 1942.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1060.

[2] *Chemist.*

quinoline was known to contain isomers. Their melting points are therefore not quite as accurate as those of the picrates, but they are sufficiently so to be serviceable for purposes of identification. Further purification would in fact serve little purpose since the styphnates melt with rather vigorous decomposition, and the highly purified trinitro-*m*-cresolates do not melt quite as sharply as do the picrates. On the other hand, even when the melting points of the picrates are very high there is never more than a one-degree difference between incipient shrinking and complete fluidity. It is the latter figure that is here recorded. An inspection of the table reveals the fact that any monomethyl- or dimethyl-quinoline can be positively identified by the preparation of its three derivatives.

It has been found that the purity of the reagents used in making the derivatives is of paramount importance. Picrates made from reagent grades of commercial picric acid melted either at a slightly lower temperature or not quite sharply, and repeated recrystallization did not serve to achieve much purification. It is conceivable that picric acid as ordinarily prepared contains a small amount of styphnic acid. The latter is more soluble in water and recrystallization of the purest commercial grades from this solvent yielded a satisfactory product (m.p. 122.6° C.)*. For the preparation of the other derivatives the styphnic acid and the trinitro-*m*-cresol were the purest commercial specimens recrystallized from hot water; they then melted at 178° C. and 109° C. respectively.

The elementary micro-analysis of the picrates for nitrogen and for carbon and hydrogen offers no difficulties. The styphnates decompose with considerable vigour and good carbon and hydrogen analyses were not obtainable, but analyses for nitrogen were not specially difficult. The trinitro-*m*-cresolates behaved like the styphnates.

The choice of derivatives alternative to the picrates was not an easy one. The flavianates are sparingly soluble well crystallized compounds, but their melting points are indefinite and too high to be useful. The picrolonates are not easily prepared and most of them are too soluble. Crystalline derivatives of 2 : 4-dinitro-phenol could not be obtained out of alcohol, and the chromates do not appear to be entirely satisfactory for analysis nor for recrystallization.

It seems advisable to point out that quinolines isolated from mixtures do not readily yield picrates of the correct melting points. When the melting point cannot be appreciably raised by further recrystallization it is advisable to regenerate the quinoline, distil, and reject end fractions. The picrate may then be recrystallized alternately from acetone–methanol, from water, and again from acetone–methanol. In most cases the solubility in boiling methanol is too low for convenient recrystallization except when the quantity is very small. There have been many occasions to determine the melting points of known mixtures of picrates and other derivatives. It was invariably found that the melting point depression was sufficient to be easily recognized. For example, a mixture of the picrates of 4 : 5- and of 4 : 8-dimethyl-quinoline is completely liquid at 205 to 210° C. and a mixture of the trinitro-*m*-cresolates of 2- and of 3-methyl-quinoline melted completely at 203° C.

---

* *All melting points are corrected.*

TABLE I

MELTING POINTS OF MONOMETHYL- AND DIMETHYL-QUINOLINE DERIVATIVES

Quinolines and their melting points	Picrate, m.p., °C.	Styphnate, m.p., °C.	Trinitro-*m*-cresolate, m.p., °C.
2-Methyl	195	219	223
3-	190	190	223
4-	220	237	254
5-	223	218	214
6-	235	234	238
7-	242	242	243
8-	205	202	199
2 : 3-Dimethyl, 70°	235	243	248
2 : 4-	196	212	211
2 : 5- ††	223	207	201
2 : 6- 60°	191	200	206
2 : 7- † 61°	196	222	250
2 : 8-	183	194	209
3 : 4- 74°	221	232	237
3 : 5- ††	220	214	221
3 : 6- †† 58°	253	234	255
3 : 7- †† 80°	244	214	222
3 : 8-	210	205	208
4 : 5- †† 78°	233	227	230
4 : 6-	249	221	244
4 : 7-	230	272*	228
4 : 8- 58°	229	231	231
5 : 6- †† 50°	201	205	202
5 : 7- ††	249	247	239
5 : 8-	186	184	180
6 : 7- † 58°	278	259*	262*
6 : 8-	230	190	184
7 : 8- ††	198	179	214

† *Quinolines previously prepared but picrate not made.*
†† *Quinolines not previously known.*
* *With gradual decomposition.*

The Syntheses

There is no question but that the Skraup synthesis with its modifications has proved the most widely applicable of all syntheses for the preparation of quinolines. It was used wherever possible. Some of the necessary amines were not readily obtainable and occasionally the corresponding nitro compounds were even less available. Picric acid was used as the oxidizing agent in a number of preparations, but recently it was observed that *o*-nitrophenol offers a number of advantages. Its slight but appreciable volatility tends to dissipate some heat during the original exothermal reaction and any hydroxyquinoline formed from the amino-phenol would not distil from the alkaline solution. By using the Cohn boric acid method (5) and *o*-nitrophenol as the oxidizing agent, a yield of 91.8% was obtained in one preparation.

There has been some confusion in regard to the position of ring closure of *m*-substituted anilines where two products can be obtained (7, 24). *m*-Toluidine can give rise to both 5- and 7-methyl-quinolines and both appear to be produced. However, by far the greater proportion of the base consists of the 7-methyl compound. The 5-methyl derivative was prepared by an unambiguous route from 4-nitro-3-amino-toluene and the nitro group in the resulting 8-nitro-5-methyl-quinoline eliminated by reduction and diazotization. Similarly, 4-*o*-xylidine yielded a mixture of 5 : 6- and 6 : 7-dimethyl-quinolines (2), but the 6 : 7-isomer was readily obtained in a pure condition by direct crystallization, and the 5 : 6-isomer was obtained in a pure form from the mother liquor as its picrate. The latter was also synthesized via its 8-nitro derivative from 4-amino-5-nitro-*o*-xylene. All the other mono- and dimethyl-quinolines substituted only in the benzene nucleus were obtained without ambiguity from the appropriate amines.

The 2-methyl-quinolines containing no other substituent in the pyridine nucleus were prepared by the Doebner and v. Miller synthesis (8). The only ambiguity here is the quinoline derived from *m*-toluidine to which Decker and Remfry (7) assigned the 2 : 5-formula. That this assumption was unwarranted was shown by the preparation of 2 : 5-dimethyl-quinoline via the 8-nitro compound from 4-nitro-3-amino-toluene, and proving that it was not identical with that obtained directly from *m*-toluidine which must therefore be the 2 : 7-dimethyl-quinoline. An attempt to isolate the 2 : 5-isomer from the mother liquors of the latter synthesis was only partly successful. The picrate was ultimately obtained but it was not pure, and this is attributed to the fact that the *m*-toluidine contained small amounts of the *o*- and *p*-isomers. The 3-methyl-quinolines, exclusive of the 2 : 3-dimethyl compound, were prepared by an adaptation of the Skraup conditions to the appropriate amine and a substituted acrolein. The Shell Development Co., Emeryville, Cal., kindly provided a generous supply of α-methylacrolein from which it was possible to synthesize the necessary bases in reasonable yields. The nitro compounds corresponding to the amines and *o*-nitrophenol were used as oxidizing agents. As in other similar ring closures *m*-toluidine yielded the 7-substituted compound, namely, 3 : 7-dimethyl-quinoline, but it was possible to isolate an appreciable amount of 3 : 5-dimethyl-quinoline from the liquid fraction of the base. The 3 : 5-isomer was unambiguously synthesized via its 8-nitro derivative.

The synthesis of 3 : 4-dimethyl-quinoline was readily achieved by condensing aniline with 2-methyl-3-keto-*n*-butanol under the above conditions (2, 4). It proved to be identical with a specimen of 3 : 4-dimethyl-quinoline obtained in unsatisfactory yield by condensing *o*-amino-acetophenone with propionaldehyde (10).

The yields of the 3 : 4-dimethyl-quinolines were so good by the modified Skraup reaction that at one time an attempt was made to prepare the 3-substituted quinolines by eliminating the 4-methyl group. The condensation of 3 : 4-dimethyl-quinoline with chloral proceeded readily but hydrolysis of the condensation product with alkali yielded only a small amount of the 4-acrylic acid, most of the condensation product under our conditions regenerating the dimethyl-quinoline. Examples of alkaline hydrolysis effecting the rupture of a double bond are rare. An analogous case is recorded by Perkin and Robinson (20) who observed that boiling α-cyano-2 : 3-dimethoxy-cinnamic acid with alkali yielded 2 : 3-dimethoxy-benzaldehyde. Furthermore, oxidation of the 4-acrylic acid to the 4-carboxylic acid and decarboxylation of the latter yielded only a small amount of impure 3-methyl-quinoline.

The 4-methyl-quinolines were prepared by applying the procedure of Mikhailov (16) for the preparation of lepidine by substituting the toluidines for aniline. The 4 : 6- and 4 : 8-dimethyl compounds were obtainable without ambiguity from *p*- and *o*-toluidine respectively. The base obtained from *m*-toluidine may have contained a small amount of 4 : 5-dimethyl-quinoline, although no difficulty was encountered in obtaining the picrate of 4 : 7-dimethyl-quinoline in a pure condition.

It was shown in a preliminary experiment that pure quinoline can be isolated from the products obtained by passing 8-methoxy-quinoline over heated zinc dust in an inert atmosphere. An attempt to prepare 4 : 5-dimethyl-quinoline from its 2-hydroxy-8-methoxy derivative by the same procedure ultimately yielded a satisfactory product, but the yield was so small that it was also prepared in another way. It appears that a small amount of elimination or wandering of methyl groups occurs under these conditions, and it is not unlikely that the zinc-dust distillation of the carbostyrils suffers from the same objection. The picrates melted at a temperature appreciably higher than Ewins and King (9) have recorded for the same compounds prepared by the same method, even when allowance was made for temperature corrections. Ewins and King purified their pyrolytic products via the picrates but it now appears that their procedure was inadequate to eliminate compounds that might have been formed by the loss or wandering of a methyl group.

It was eventually demonstrated that the desired 4 : 5-dimethyl-quinoline could be prepared from 4-nitro-3-amino-toluene. This was condensed with 3-keto-*n*-butan-1-ol under the Doebner and v. Miller conditions to give a small amount of 8-nitro-4 : 5-dimethyl-quinoline. Elimination of the nitro group via the amino group gave a very small yield of the required base, which was obtained crystalline and purified as such.

At this point the possibility of removing a bromine atom from the benzene nucleus by the procedure of Girardet (11) was investigated, having in mind that it might be used to block one of the positions ortho to the amino group. For this purpose 3-methyl-6-bromo-quinoline was prepared. Reduction with the zinc-copper couple eliminated the halogen but at the same time partly reduced the quinoline. It was necessary to dehydrogenate the latter to yield 3-methyl-quinoline, which was then relatively pure.

The 2 : 3-dimethyl-quinoline was prepared by condensing isatoic acid with methyl-ethyl ketone and decarboxylating the resulting 2 : 3-dimethyl-quinoline-4-carboxylic acid. The synthesis of 2 : 4-dimethyl-quinoline from *o*-amino-acetophenone and acetone proved to be impracticable both on account of the poor yield and the difficulty of obtaining a pure substance. The Skraup reaction when applied to aniline and 4-keto-pentan-2-ol yielded the desired substance in a satisfactory state of purity (13).

Incidentally, 7-ethyl-quinoline and a number of trimethyl-quinolines have been prepared and are described in the experimental section.

All crystalline new compounds here described were analysed for at least one element. Where the properties of previously known substances varied by more than a reasonable amount from recorded values they were also analyzed. It remains to be added that all the melting points were determined in a sulphuric acid bath with Anschütz thermometers and are therefore practically corrected. The apparatus has repeatedly been checked with compounds of known melting points. After an approximate value had been determined, the value was more accurately determined, the rate of heating being decreased as the melting point was reached. The fresh sample was placed in the bath at a temperature about 20° C. below its melting point. All recorded melting points have been checked a number of times and one of the writers (R.H.F.M.) has determined the melting points of all picrates on at least two occasions.

It is deemed impracticable to give all the references relevant to the many published researches upon which this work is based. Such a list would add greatly to the length of the present paper. It also seemed unnecessary to cite the many values for the melting points of the bases and the picrates as recorded by previous investigators.

Experimental

As progress from one preparation to the next was made, a great deal was learnt about the many reactions that were used. It is therefore obvious that the yields were not always the maximum attainable. For this reason it is deemed expedient to select only a few typical experiments for detailed description. In these the yields are probably the best that can be achieved unless some new procedure is discovered.

When the quinoline itself was a solid at room temperature it was recrystallized from specially purified hexane until there was no further increase in melting point.

The picrates were prepared by adding a hot methanolic solution of the quinoline to a solution of excess picric acid in hot methanol. In general, the picrate was filtered off while the mixture was still warm, and washed with methanol. The picrate was then recrystallized either from boiling methanol or from a mixture of acetone and methanol. With the single exception of 7-methyl-quinoline picrate there was no appreciable increase in the melting points of the picrates on recrystallization. The styphnates and trinitro-*m*-cresolates were prepared exactly as the picrates, but only the 7-methyl-quinoline derivatives were recrystallized.

The Skraup Syntheses

The following synthesis is one employing the Cohn boric acid method (5) but instead of using the nitro compound corresponding to the amine, *o*-nitrophenol was used as the oxidizing agent. Its use in this connection appears to be new. It possesses distinct advantages over picric acid, which was also used in a number of syntheses. Its ready solubility in the sulphuric acid brings it into intimate contact with the reactants, and, owing to its volatility, it acts as a heat sink, and when the reaction is completed the excess can easily be removed by steam distillation.

7-Ethyl-quinoline

To a mixture of 3.5 gm. of ferrous sulphate, 12 gm. of *m*-ethyl-aniline, 8.3 gm. of *o*-nitrophenol, and 6.5 gm. of boric acid dissolved in 37.5 gm. of glycerol was added slowly and with shaking 18 cc. of concentrated sulphuric acid. The mixture was gradually heated to boiling and then boiled under reflux for three hours. At no time was there any evidence of a violent reaction.

The somewhat diluted mixture was distilled in a current of steam to remove the excess nitrophenol, made alkaline, and the quinoline was then distilled in steam. The base obtained from the distillate was purified in the usual manner by diazotization, etc. There was obtained 14.6 gm. of 7-ethyl-quinoline presumably contaminated with a small amount of 5-ethyl-quinoline. This corresponds to a yield of 91.8% based upon the *m*-ethyl-aniline, and the writers believe that it is the highest ever recorded for a Skraup synthesis.

The picrate was recrystallized twice from acetone-methanol; m.p. 229° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.71%. The styphnate melted at 268° C. and the trinitro-*m*-cresolate at 240° C.

8-Nitro-5-methyl-quinoline

A mixture of 25 gm. of ferrous sulphate, 15 gm. of 4-nitro-3-acetylamino-toluene, 3 gm. of picric acid, 26 cc. of glycerol, 4 gm. of boric acid, and 11 cc. of sulphuric acid was boiled for 3.5 hr. The 8-nitro-5-methyl-quinoline was isolated as in the case of the corresponding 5 : 6-dimethyl-quinoline derivative (*vide infra*) and recrystallized three times from hot ethanol.

There was obtained 3.2 gm. of the compound, which melted at 138° C. Calc. for $C_{10}H_8O_2N_2$: N, 14.89%. Found: N, 14.95%.

The 3-amino-4-nitro-toluene required in this and later syntheses was prepared from *m*-cresol (25) through the following stages,—3-hydroxy-4-nitro-toluene (m.p. 56° C.), 3-ethoxy-4-nitro-toluene (m.p. 52° C.), and 3-amino-4-nitro-toluene (m.p. 112° C.). The last stage was carried out in an autoclave with aqueous ammonia and a little ethanol (12). The yield was 59%.

5-Methyl-quinoline

The reduction of 8-nitro-5-methyl-quinoline (3.17 gm.) with iron and hydrochloric acid yielded the sparingly soluble hydrochloride of 8-amino-5-methyl-quinoline in dark red prisms, which began to char at 200° C. The free base (1.65 gm.) was obtained as a pale yellow oil, b.p. 115° (1.5 mm.).

The picrate was obtained in brilliant red needles melting at 234° C. Calc. for $C_{16}H_{13}O_7N_5$: C, 49.62; H, 3.36; N, 18.09%. Found: C, 49.99; H, 3.72; N, 18.29%.

The amino-quinoline (1.63 gm.) was diazotized in hydrochloric acid and then treated with hypophosphorous acid (15). The basified solution was distilled in a current of steam and the quinoline distilled twice *in vacuo*, b.p. 85° (1 mm.); yield, 1.03 gm. It was obtained as an almost colourless oil, which yielded a picrate moderately soluble in boiling methanol. Calc. for $C_{16}H_{12}O_7N_4$: N, 15.05%. Found: N, 15.00%.

6-Methyl-, 7-Methyl-, and 8-Methyl-quinoline

These three methyl-quinolines were prepared by the Clarke and Davis (4) procedure from the requisite toluidines, which had been previously distilled. The quinolines were repeatedly distilled *in vacuo*. The 6- and 8-methyl-quinolines yielded pure picrates without further recrystallization. The picrate of 7-methyl-quinoline as prepared in methanol melted at 235° C. When recrystallized twice more from acetone-methanol it melted at 242° C. and further recrystallization did not alter this value. Calc. for $C_{16}H_{12}O_7N_4$: N, 15.05%. Found: N, 15.10%.

The styphnate of 7-methyl-quinoline was recrystallized twice from acetone-methanol. It consisted of fine colourless prisms melting with vigorous decomposition at 242° C. Calc. $C_{16}H_{12}O_8N_4$: N, 14.43%. Found: N, 14.45%.

The trinitro-*m*-cresolate was obtained in fine yellow prisms with a greenish cast. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.55%.

5 : 7-Dimethyl-quinoline

This quinoline was prepared by the procedure of Clarke and Davis (4). There was used 14.4 gm. of ferrous sulphate, 38 gm. of 5-nitro-1 : 3-dimethyl-benzene, 50 gm. of 5-amino-1 : 3-dimethyl-benzene, 123 cc. of glycerol, and 72 cc. of sulphuric acid. Gentle heating brought about an exothermal reaction that kept the mixture boiling for 15 min., after which it was boiled for four hours.

The quinoline was isolated in the usual way; it weighed 4.8 gm. On cooling, the base yielded a colourless mass of crystals that melted at 22° C. For the preparation of its picrate it was redistilled twice, large end fractions being rejected. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.63; N, 14.51%. Found: C, 52.79; H, 3.73; N, 14.58%.

5 : 8-Dimethyl-quinoline

The 2-amino-*p*-xylene required for the 5 : 8-compound was isolated from commercial xylidine as hydrochloride, and this was recrystallized several times from dilute hydrochloric acid (18). The quinoline (Skraup) was obtained as an almost colourless oil, which on cooling formed a colourless solid that remelted at 2° C. The picrate was analysed. Calc. for $C_{17}H_{14}O_7N_4$: N. 14.51%. Found: N, 14.46%.

6 : 7-Dimethyl-quinoline

The 4-amino-*o*-xylene required for the preparation of the 6 : 7-base was prepared from crystalline 4-nitro-*o*-xylene (6), purified as its acetyl derivative, and used as such. The yield of redistilled quinoline (Skraup) was 67% of the theoretical. It solidified on cooling, leaving a small amount of oil that was removed by prolonged draining at the pump (2). The solid was recrystallized twice from purified hexane; it then melted at 58° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 9.14%. The colourless stout prisms possess an odour suggestive of camphor as well as of quinoline. The picrate was prepared from the recrystallized base. It was virtually insoluble in hot methanol and only very sparingly soluble in boiling acetone, from which solvent a small amount was recrystallized with unaltered melting point. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85, H, 3.63%. Found: C, 53.05; H, 3.97%.

The oil from which the 6 : 7-dimethyl-quinoline had been filtered was dissolved in a large volume of hot methanol, and the solution treated with a hot methanolic solution of picric acid in slight excess. The solid that separated consisted largely of the picrate of the 6 : 7-base. It was filtered hot and the picrate, which crystallized from the cooled filtrate, was recrystallized from acetone–methanol until the melting point was sharp and constant at 201° C. The picrate was then completely soluble in either hot methanol or hot acetone and when admixed with a specimen of 5 : 6-dimethyl-quinoline picrate prepared as described below it melted at 201° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.59%.

The free base was regenerated from the picrate by shaking the latter with ammonia in the presence of ether. The solvent was removed from the washed extract and the residue distilled. On cooling, it solidified at once and when recrystallized from hexane it melted sharply at 50° C. The picrate prepared from the crystalline base also melted at 201° C. There was isolated about 1.4 gm. of this base from 20 gm. of the mixture.

8-Nitro-5 : 6-dimethyl-quinoline

A mixture of 9.7 gm. of ferrous sulphate, 60 gm. of 5-nitro-4-acetylamino-1 : 2-dimethylbenzene (19), 12 gm. of picric acid, and a solution of 17 gm. of boric acid in 82 gm. of glycerol, was treated with 44 cc. of sulphuric acid, and boiled under reflux for 3.5 hr.

The cooled and diluted solution was filtered to remove some resin and then basified with caustic soda. The filtered and washed precipitate was extracted with a hot 1 : 1 alcohol-benzene mixture. The solvent was removed from the extract and the solid residue distilled *in vacuo*. There was obtained 10 gm. of a pale yellow solid, which, when recrystallized from hot methanol, melted sharply at 166°. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%. Found: N, 13.76%.

When the nitro-quinoline was reduced with stannous chloride in the presence of hydrochloric acid, a sparingly soluble stannichloride was formed. This was decomposed only slowly in the presence of sodium hydroxide. The recovered base was extracted with benzene, distilled *in vacuo*, and recrystallized from methanol; m.p. 78 to 79° C. The mono-picrate crystallized from methanol in orange coloured needles melting at 213° C. Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%. Found: N, 17.28%.

5 : 6-Dimethyl-quinoline

When this quinoline was prepared from its 8-amino derivative the authors were not acquainted with the hypophosphorous acid reduction of diazonium compounds (cf. preparation of 5-methyl quinoline). A solution of 2 gm. of 8-amino-5 : 6-dimethyl-quinoline in 20 cc. of ethanol and 0.5 cc. of sulphuric acid was diazotized in the cold with a saturated aqueous solution of sodium nitrite and then heated on the steam-bath to complete the reaction and to remove the acetaldehyde and most of the alcohol. The solution was then treated with sodium hydroxide and distilled in a current of steam. The distillate was extracted with benzene and the residue from this solvent distilled *in vacuo*. There was obtained a low boiling fraction (about 90° (3 mm.)), which was converted into its picrate. This, when recrystallized from methanol, melted sharply at 201° C. either alone or in admixture with the above described picrate of 5 : 6-dimethyl-quinoline.

The higher boiling fraction was also converted into its picrate and this recrystallized from methanol; m.p. 224° C. Analysis indicates that it is the picrate of 8-ethoxy-5 : 6-dimethyl-quinoline. Calc. for $C_{19}H_{18}O_8N_4$: N, 13.02%. Found: N, 13.60%.

6 : 8-Dimethyl-quinoline

This base was obtained in 70% yield (Skraup) from 4-*m*-xylidine, which was purified via its acetate (18). The quinoline was redistilled a number of times, liberal end fractions being discarded.

7 : 8-Dimethyl-quinoline

The procedure of Clarke and Davis gave a 50% yield. The 3-amino-*o*-xylene was prepared from a specimen of 3-nitro-*o*-xylene that had been exhaustively fractionated to eliminate the 4-nitro isomer. The quinoline was redistilled three times, each time without actual boiling of the liquid. The picrate was analysed. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.52%.

2-Methyl-quinoline (Quinaldine)

Quinaldine and the other 2-methyl-quinolines (except the 2 : 3- and the 2 : 4-compounds) were prepared by the Doebner and v. Miller synthesis as modified by Mills, Harris, and Lambourne (17). The quinaldine itself was redistilled a number of times and the fraction boiling at 110° (6 mm.) collected separately.

2 : 5-Dimethyl-quinoline

The substitution of 3-amino-4-nitro-toluene (12) for aniline in the procedure of Mills, Harris, and Lambourne (17) for the synthesis of quinaldine yielded 8-nitro-2 : 5-dimethyl-quinoline. The cooled and diluted reaction mixture was filtered to remove the resins, basified with sodium hydroxide, and the solid nitro base filtered, washed with water, dried, and sublimed *in vacuo* (140 to 160° (1.5 mm.)). It was recrystallized from boiling methanol from which it separated as long, stout, white needles melting at 174° C. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%. Found: N, 13.82%.

8-Nitro-2 : 5-dimethyl-quinoline (3 gm.) when reduced with iron and alcoholic hydrochloric acid yielded 8-amino-2 : 5-dimethyl-quinoline as a yellowish oil, b.p. 110 to 115° (1.5 mm.), weighing 1.93 gm. A small quantity was converted to the picrate, which, after recrystallization from methanol, consisted of small bright red prisms, m.p. 189°. Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%. Found: N, 17.49%.

Treatment of diazotized 8-amino-2 : 5-dimethyl-quinoline (1.90 gm.) with hypophosphorous acid according to Mai's procedure (14) yielded 2 : 5-dimethyl-quinoline as an oil, b.p. 80 to 85° (1 mm.) (1.01 gm.). The picrate was obtained from methanol in slender, soft, yellow needles. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.32, 14.35%.

2 : 6-Dimethyl-quinoline

This substance was prepared by the method of Mills, Harris, and Lambourne (17), in which *p*-toluidine (175 gm.) was substituted for aniline. There was obtained 75 gm. of distilled oil, b.p. 104° C. (1 mm.), which crystallized on cooling. The crystalline 2 : 6-dimethyl-quinoline was separated from a small quantity of oil by filtration through a fritted glass funnel. After two recrystallizations from petroleum ether it was obtained as small, stout prisms, melting at 60°. The picrate formed in methanol is dimorphous. It separated first in small crystals that melted indefinitely between 187 and 191°, but on standing in the presence of methanol the crystals changed to a larger form melting sharply at 191°. The higher melting form is obtained when either form is recrystallized from hot acetone-methanol

2 : 7-Dimethyl-quinoline

This base was prepared from *m*-toluidine, paraldehyde, and concentrated hydrochloric acid, as described by Doebner and v. Miller (8). The product consisted of an oil, b.p. 115 to 116° C. (7 mm.), which largely solidified on cooling in the refrigerator. The crystals were separated from the adhering oil by filtration on a fritted glass funnel and then recrystallized from petroleum ether, m.p. 61°.

The filtered oil was converted to the picrate. From the more soluble fraction an impure picrate melting indefinitely at 205 to 210° C. was obtained. This was achieved by alternately recrystallizing the more soluble fractions from methanol and from water.

2 : 8-Dimethyl-quinoline

This quinoline was obtained by the method of Mills, Harris, and Lambourne (17), using *o*-toluidine instead of aniline. It consists of a straw-coloured oil, b.p. 93 to 95° (2 mm.). The trinitro-*m*-cresolate was obtained in yellow rectangular plates, which on exposure to light assumed a grey colour. This colour change did not affect the melting point.

2 : 3-Dimethyl-quinoline

This was prepared from isatin and methyl-ethyl-ketone by the method of Pfitzinger (21) as modified by Plant and Rosser (22). It is a solid that crystallizes from petroleum ether, m.p. 70.5°. The picrate separates from methanol in short, stout, yellow prisms. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.50%.

2 : 3 : 6-Trimethyl-quinoline

The starting material for this synthesis was 5-methyl-isatin, m.p. 187° C., prepared in 88.2% yield from *p*-toluidine by the method of Sandmeyer as described in "Organic Syntheses" (15). The 5-methyl-isatin was condensed with methyl-ethyl-ketone as in the preparation of 2 : 3-dimethyl-quinoline. The 2 : 3 : 6-trimethyl-quinoline-4-carboxylic acid (38% yield) was dried and decarboxylated by distillation. 2 : 3 : 6-Trimethyl-quinoline distilled as a heavy oil that crystallized immediately. After two recrystallizations from petroleum ether it had a constant melting point of 87.5°. The picrate, prepared in methanol, separated as lemon-yellow leaflets, m.p. 217°. The styphnate and the trinitro-*m*-cresolate melted at 238° and at 224° respectively.

2 : 3 : 8-Trimethyl-quinoline

This was prepared from 7-methyl-isatin (m.p. 275° C., obtained from *o*-toluidine in 23.4% yield) by condensation with methyl-ethyl-ketone. The 2 : 3 : 8-trimethyl-quinoline-4-carboxylic acid (23% yield) thus produced was decarboxylated by distillation at atmospheric pressure. 2 : 3 : 8-Trimethyl-quinoline was obtained as a heavy oil that crystallized immediately, b.p. 85 to 95° (1 mm.). After two recrystallizations from petroleum ether it separated as colourless prisms melting at 56 to 57°. The picrate crystallized from methanol as light yellow needles melting at 252°. The styphnate and the trinitro-*m*-cresolate melted at 239° and at 227° respectively.

2 : 4-Dimethyl-quinoline

To a mixture of 10 gm. of ferrous sulphate, 25 gm. of aniline, 17 gm. of nitrobenzene, and 30 cc. of sulphuric acid, which was maintained at 160° C., was added dropwise 25 gm. of 4-keto-pentan-2-ol (prepared by condensing acetone with acetaldehyde (3)). After heating under gentle reflux for 6.5 hr. the quinoline was isolated from the reaction products as in the Skraup procedure. There was obtained 8 gm. of a colourless product of constant boiling point.

The picrate prepared from a middle fraction was moderately soluble in hot methanol, from which it was obtained in brilliant yellow plates.

The yield of 2 : 4-dimethyl-quinoline by condensing acetone with *o*-amino-acetophenone was very poor (10). Nevertheless, there was obtained a sufficient quantity of the base to permit adequate purification of it and recrystallization of the picrate to constant melting point (196° C.).

3-Methyl-quinoline

Method I. A gently boiling mixture of ferrous sulphate (4 gm.), aniline (8 gm.), nitrobenzene (7.0 gm.), and sulphuric acid (15 cc.) was slowly heated with α-methylacrolein dimethyl-acetal (10 gm.) (27) and heating continued for several hours. The quinoline was isolated in the usual way and converted to the picrate, which, when twice recrystallized, melted at 188° C.

Method II. The procedure used was that employed in the preparation of 3 : 7-dimethyl-quinoline. From 15 gm. of ferrous sulphate, 33 gm. of aniline, 20 gm. of *o*-nitrophenol, 44 cc. of sulphuric acid, and 32 gm. of α-methylacrolein, there was obtained 20 gm. of once distilled 3-methyl-quinoline. For the preparation of the picrate and other derivatives the base was redistilled twice, the last time 1 gm. being collected from the middle fraction. The picrate melted at once at 190° C. and recrystallization did not raise this value.

3 : 4-Dimethyl-quinoline

Method I. (Camps' synthesis). A mixture of 5 gm. of *o*-amino-acetophenone and 3 gm. of propionaldehyde was heated to 225° C. for one hour in a sealed tube. The acidified product (dilute sulphuric acid) was distilled in a current of steam, cooled, diazotized, distilled in steam, basified with sodium hydroxide, and again distilled in steam. The distillate yielded to benzene extraction a small amount of oil, which, when distilled, weighed 0.5 gm. The picrate was moderately soluble in boiling methanol or acetone. It melted sharply at 221° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.63%.

Method II. The procedure adopted for the preparation of 2 : 4-dimethylquinoline was followed except that 2-methyl-3-keto-*n*-butanol was reacted with aniline (25 gm.), nitrobenzene (17 gm.) sulphuric acid (30 cc.) and ferrous sulphate (10 gm.). There was obtained 18 gm. of a colourless distillate that crystallized almost completely on cooling. After two recrystallizations from hexane it melted sharply at 74° C. The picrate prepared from this melted before and after recrystallization at 221° C., and in admixture with that prepared as described above it melted at the same temperature. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.35%.

γ,γ,γ-Trichloro-α-(3-methyl-4-quinolyl)-propene

A mixture of 3 : 4-dimethyl-quinoline and a slight excess of chloral hydrate was heated on the steam bath with a pellet of anhydrous zinc chloride. In the course of 30 min. the mixture became solid. It was ground in a mortar with cold methanol and the solid, after filtering and washing with methanol, was recrystallized from a large volume of the same solvent. Colourless hard prisms of the trichloro-quinolyl-propene melting at 218° C. were thus obtained. Calc. for $C_{13}H_{10}NCl_3$: N, 4.89%. Found: N, 4.75%. The yield was nearly quantitative.

8-Nitro-3 : 5-dimethyl-quinoline

To a solution of 15 gm. of 3-amino-4-nitro-toluene in 44 cc. of concentrated hydrochloric acid cooled to 0° C. was slowly added 15 gm. of α-methylacrolein. The mixture was allowed to come to room temperature, and after 30 min., 9 gm. of zinc chloride was added and the whole boiled under reflux for five hours. The cooled solution was filtered to remove gums and basified with sodium hydroxide. The precipitated base was filtered off, dried, and distilled *in vacuo*. The crystalline distillate was recrystallized from methanol; it yielded 114 mg. of virtually colourless crystals of 8-nitro-3 : 5-dimethyl-quinoline melting at 192° C. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.85%. Found: N, 13.69%.

An attempt to prepare the same quinoline by using the Skraup conditions, but substituting α-methylacrolein for glycerol, gave the same substance. The yield was about the same as in the modified Doebner and v. Miller conditions described above.

8-Amino-3 : 5-dimethyl-quinoline

A solution of 150 mg. of 8-nitro-3 : 5-dimethyl-quinoline in 3 cc. of ethanol containing 0.1 cc. of hydrochloric acid was treated with 116 mg. of iron powder and boiled for 2.5 hr. The mixture was filtered and the insoluble residue washed with alcohol. The filtrate was evaporated somewhat, basified with sodium hydroxide, and extracted with ether. The alcohol insoluble residue was dissolved in dilute acid, the solution basified, and extracted with ether. The two ether extracts were combined, the solvent was removed, and the residue distilled *in vacuo*. There was obtained 93 mg. of an almost colourless crystalline distillate. A small portion was converted into its picrate, which, when recrystallized from methanol, melted at 214° C. Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%. Found: N, 17.36%.

3 : 5-Dimethyl-quinoline

The 8-amino derivative of this quinoline was diazotized and the diazo solution treated with an excess of hypophosphorous acid. After it had remained for about 15 hr. in the ice chest the solution was made alkaline and distilled in a current of steam. The colourless oil yielded a picrate which was moderately soluble in hot acetone or methanol. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.60%.

3 : 6-Dimethyl-quinoline

This base was prepared by the procedure outlined in the case of the 3 : 7-compound except that *p*-nitro-toluene was used instead of *o*-nitrophenol as the oxidizing agent. From 38 gm. of *p*-toluidine there was obtained 6.5 gm. of colourless crystalline base, which, when recrystallized twice from hexane, melted sharply at 58° C. Calc. for $C_{11}H_{11}N$: C, 84.08; H, 7.00%. Found: C, 84.10, 84.30; H, 6.76, 6.90%.

The picrate was rather sparingly soluble in hot methanol or acetone. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.53%.

3 : 7-Dimethyl-quinoline

In this preparation the writers were interested not only in obtaining the 3 : 7-base but also in isolating the small amount of accompanying 3 : 5-compound. Attempts to isolate pure 2 : 5-dimethyl-quinoline from the more abundant 2 : 7-dimethyl-quinoline formed in the Doebner and v. Miller synthesis of the latter from *m*-toluidine were only partially successful. A completely pure picrate could not be isolated by fractional crystallization.

This failure is attributed to the fact that we used a commercial specimen of *m*-toluidine that may have contained small amounts of the *o*- and *p*-isomers, and in consequence the bases in the mother liquor probably consisted of no fewer than four quinolines. In order therefore to be certain of the purity of the *m*-toluidine it was prepared from 3-nitro-4-amino-toluene by first eliminating the amino group and then reducing the *m*-nitro-toluene. The writers took the added precaution of distilling both the nitro compound and the toluidine through a Widmer column, arbitrarily discarding liberal amounts of end fractions.

To a mixture of 40 gm. of ferrous sulphate, 101 gm. of *m*-toluidine, 47 gm. of *o*-nitrophenol, and 105 cc. of sulphuric acid maintained at 140° C. was added 87 gm. of α-methylacrolein in the course of about 10 minutes. It was then heated under reflux for 3.5 hr., diluted with water, and distilled in a current of steam to remove the excess *o*-nitrophenol. The basified solution (sodium hydroxide) was again distilled with steam and the volatile base purified as in the case of the 7-ethyl-quinoline. There was obtained 50 gm. of a pale greenish distillate that crystallized for the greater part, b.p. 101 to 103° (1 mm.) The oil was drained off and the solid recrystallized twice from purified hexane. It was obtained in colourless stout prisms melting sharply at 80° C. Calc. for $C_{11}H_{11}N$: C, 84.08; H, 7.00%. Found: C, 84.05; H, 6.92%.

The picrate, prepared from the recrystallized 3 : 7-dimethyl-quinoline, was only sparingly soluble even in boiling acetone. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.51%.

The oily mixture from which the crystalline base had crystallized was redistilled, cooled in the ice chest, and the oil drained from the crystals on a fritted glass filter. Owing to the fact that the picrate of 3 : 5-dimethyl-quinoline is more soluble in methanol and in acetone than that of the 3 : 7-isomer, it was attempted to eliminate the latter by fractional precipitation. A certain amount of separation was accomplished but the picrate from the more soluble fractions melted indefinitely at 210° C. after repeated recrystallization. That it consisted largely of the 3 : 5-compound was shown by the fact that in admixture with the pure 3 : 5-picrate it was completely liquid only at 215° C.

While searching for other derivatives suitable for separating these bases the writers observed that the perchlorate of 3 : 7-dimethyl-quinoline crystallizes rather well but is quite soluble even in cold water. The bases were therefore recovered from their picrates and dissolved in hot dilute perchloric acid. Even while the mixture was still warm a sparingly soluble perchlorate crystallized from the solution. This was filtered off (the quinoline regenerated from the filtrate crystallized at once; after pressing out on filter paper it melted at 78° C. and in admixture with 3 : 7-dimethyl-quinoline it melted at 79° C.), washed with cold water, and recrystallized from boiling water in which it is readily soluble. The brilliant colourless prisms obtained by filtering, washing, and drying melted sharply at 216° C. Calc. for $C_{11}H_{11}N \cdot HClO_4$: N, 5.44%. Found: N, 5.40%.

The base regenerated from the perchlorate was distilled *in vacuo* and obtained as a brilliantly colourless liquid that set to a glass on cooling to −80° C. When this was allowed to come to room temperature there was a temporary appearance of crystals at the junction between the glassy solid and the liquid base. The picrate prepared in methanol from this base melted sharply at 220° C. either alone or in admixture with the picrate of the authentic specimen of 3 : 5-dimethyl-quinoline. Recrystallization failed to raise this melting point.

The yield of pure base was almost 5 gm. Since the separation was not entirely quantitative it is reasonable to assume that the 3 : 5-isomer constituted about 10 to 12% of the total mixture.

m-Toluidine

A mixture of 350 cc. of hydrochloric acid in one litre of water and 228 gm. of 4-amino-3-nitro-toluene was diazotized at 10 to 13° C. with a solution of 105 gm. of sodium nitrite in 450 cc. of water. The excess of nitrous acid was removed by the addition of sulphamic acid and the solution was then treated with 250 gm. of 30% hypophosphorous acid cooled to 0° C. This amount of hypophosphorous acid is much less than that used by Mai (14) or by Adams and Kornblum (1), but in our experience the yields are not increased by augmenting the quantity of acid. The cold mixture was allowed to come to room temperature in the course of six hours, allowed to remain overnight, and distilled in a current of steam. The *m*-nitro-toluene was extracted with benzene, washed with 10% sodium hydroxide solution, and the solvent removed. The residual oil, which weighed 164 gm., was slowly distilled *in vacuo* through a Widmer column. Copious end fractions were discarded. The fraction boiling at 57° C. (1 mm.) weighed 143 gm. (70% yield).

The amine was prepared from this by reduction with iron filings and acetic acid. It was also purified by slow distillation through a Widmer column.

3 : 8-Dimethyl-quinoline

This base was prepared by the procedure used for the 3 : 7-compound except that *o*-nitro-toluene was used as the oxidizing agent. The yield was 10 gm. of twice distilled base from 38 gm. of *o*-toluidine. It crystallized on chilling in ice but was liquid at room temperature. Calc. for $C_{11}H_{11}N$: C, 84.08; H, 7.00%. Found: C, 84.17; H, 7.28%.

The picrate was moderately soluble in boiling methanol or acetone. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.64%.

3 : 4 : 7-Trimethyl-quinoline

The procedure adopted for the preparation of the 3 : 4-dimethyl-quinoline gave such good yields of otherwise difficultly accessible quinolines that its applicability to other amines was tested. There was also the possibility of eliminating the 4-methyl group and thus obtain a variety of 3-methyl-quinolines. These were ultimately obtained by a direct route so that the more involved procedure was abandoned. When molecular equivalents of *m*-toluidine (28 gm.) and *m*-nitro-toluene were substituted for the aniline and the nitrobenzene there was obtained 12 gm. of a colourless oil which crystallized for the greater part. The oil was removed on porous plate and the base recrystallized twice from hexane. It melted sharply at 78° C. Calc. for $C_{12}H_{13}N$: N, 8.10%. Found: N, 7.98%.

The picrate, prepared from the purified quinoline, melted sharply at 229° C. either before or after recrystallization from acetone-methanol. Calc. for $C_{18}H_{16}O_7N_4$: N, 14.00%. Found: N, 14.14, 14.12%. The styphnate and the trinitro-*m*-cresolate melted at 234° C. and 218° C. respectively.

3-Methyl-6-bromo-quinoline and its Debromination

The reactants and conditions for synthesizing this bromo-quinoline were the same as those used for the preparation of 3 : 7-dimethyl-quinoline except that *p*-bromo-aniline was substituted for *m*-toluidine. From 30 gm. of the aniline there was obtained 5 gm. of colourless fine needles of 3-methyl-6-bromo-quinoline, which, when recrystallized from hexane, melted at 103° C. Calc. for $C_{10}H_8NBr$: C, 54.05; H, 3.60; N, 6.31%. Found: C, 54.55; H, 3.67; N, 5.94%. The picrate was only very sparingly soluble in hot methanol, and it melted at 235° C. Calc. for $C_{16}H_{11}O_7N_4Br$: N, 12.42%. Found: N, 11.62%.

The bromo-quinoline (2.2 gm.) in ethanol (25 cc.) was boiled under reflux for three hours with 8 gm. of zinc-copper couple and sodium hydroxide (3 gm.) in a little water. The mixture was then distilled in a current of steam, the quinoline in the distillate extracted with benzene, and ultimately distilled *in vacuo*. The fraction boiling below 95° C. (1 mm.) yielded an orange coloured picrate of indefinite melting point. It was therefore heated with palladium–barium-sulphate in an atmosphere of hydrogen (200° C. for three hours). The product was redistilled to yield about 0.15 gm. of a colourless oil that gave a pure yellow picrate melting at 189° C. In admixture with an authentic specimen of 3-methyl-quinoline picrate it also melted at the same temperature.

4-Methyl-quinoline (Lepidine)

The synthesis of carbostyrils by the method of Knorr (13) gave good yields if the intermediate aceto-acetanilide was obtained in a state of moderate purity. It is frequently advantageous to dissolve the reaction product of ethyl acetoacetate and the aniline in ether and wash with dilute hydrochloric acid. Removal of the ether yields an oil that crystallizes readily. The solid may then be washed with a little petroleum ether. From 192 gm. of *p*-toluidine and 240 gm. of ethyl acetoacetate there was obtained 190 gm. of pure acetoacet-*p*-toluidide.

The conversion of the carbostyril into the corresponding quinoline by heating with zinc dust in an atmosphere of hydrogen (9) is not as satisfactory as the procedure of Mikhailov (16) who first converted the carbostyril into the 2-chloroquinoline by means of phosphorus oxychloride and reduced this with tin and hydrochloric acid. By this method there was obtained 25 gm. of twice distilled lepidine from 58 gm. of 4-methyl-carbostyril. There is the possibility that the reduction with tin and hydrochloric acid may lead to the formation of tetrahydroquinolines. These, however, yield orange coloured picrates and with nitric acid they give an immediate intense blood red colour. None of the 4-methyl-quinolines gave either test. It is probable that the zinc dust procedure may result in the elimination or wandering of methyl groups. Otherwise it is difficult to account for the low melting points recorded by Ewins and King (9).

4 : 6-Dimethyl-quinoline

Reduction of 54 gm. of 4 : 6 dimethyl-2-chloroquinoline with 33.5 gm. of tin and 250 cc. of concentrated hydrochloric acid in 335 cc. of water yielded 27 gm. of pure 4 : 6-dimethyl-quinoline. Ewins and King give m.p. 230° C. (? corr.) for the picrate. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.62, 14.44%.

4 : 7-Dimethyl-quinoline

Owing to the possibility of also obtaining a small amount of 4 : 5-dimethyl-quinoline in this synthesis the intermediate 2-chloro-quinoline was distilled a second time. From 96 gm. of *m*-toluidine there was obtained 12 gm. of three times distilled 4 : 7-dimethyl-quinoline. The picrate was analysed. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.46%.

4 : 8-Dimethyl-quinoline

From 192 gm. of *o*-toluidine 35 gm. of the purified quinoline was obtained. Although this quinoline did not crystallize when placed in the ice chest it ultimately crystallized at room temperature. A small amount of oil was removed by pressing out on filter paper. The recrystallized base melted sharply at 58° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 8.91%. The picrate obtained in brilliant plates was moderately soluble in boiling methanol. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.50%.

4 : 5-Dimethyl-quinoline

Method I

The 3-amino-4-methoxy-toluene was obtained by reducing 3-nitro-4-methoxy-toluene with iron and hydrochloric acid. The amino compound (27.1 gm.) was condensed with ethyl acetoacetate (30 gm.) (9) and the crystalline acetoacet-3-methyl-6-methoxy-anilide (38 gm.) recrystallized from ether-hexane; m.p. 81° C. Calc. for $C_{12}H_{15}O_3N$: N, 6.33%. Found: N, 6.26%. Ring closure was effected in sulphuric acid by the method of Mikhailov (16). The 2-hydroxy-8-methoxy-4 : 5-dimethyl-quinoline, obtained in 86% yield, was recrystallized from aqueous methanol, giving colourless glistening needles that melted at 219° C. Calc. for $C_{12}H_{13}O_2N$: N, 6.89%. Found: N, 6.82%.

Elimination of both the hydroxyl- and the methoxyl-groups proved to be very wasteful. It was achieved in one step by distillation over zinc dust in a current of hydrogen at a temperature of 440° C. There was obtained 18 gm. of crude distillate from 52 gm. of carbostyril. The product was distilled, yielding 9.5 gm. of oil boiling at 165 to 180° C. (10 mm.). The distillate was dissolved in ether, washed with aqueous sodium hydroxide, and the recovered oil redistilled. The fraction boiling at 125 to 130° (3 mm.) was converted into its picrate, which was systematically recrystallized from acetone-methanol until it melted not quite sharply at 225° C. The quinoline was regenerated from this picrate and distilled. The fraction that distilled at 85 to 90° (1 mm.) crystallized on cooling. It was pressed out on filter paper and recrystallized from hexane. The colourless plates thus obtained melted at 76 to 77° C. The picrate prepared from this product was only sparingly soluble, and it melted at 233° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.53%.

Method II

The condensation of 3-amino-4-nitro-toluene (22 gm.) with 3-keto-*n*-butanol (20 gm.) under the conditions of the Doebner and von Miller synthesis was carried out by the Mills, Harris, and Lambourne (17) procedure. The cooled, diluted, and filtered reaction mixture was basified with an excess of sodium hydroxide. The precipitated base was filtered off, washed, dried, and distilled *in vacuo*. The reddish coloured oil, boiling at 170 to 180° C. (2 mm.), weighed 4.16 gm.; it crystallized on cooling. It was recrystallized from boiling methanol and the 8-nitro-4 : 5-dimethyl-quinoline thus obtained consisted of colourless needles melting at 140° C. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%. Found: N, 14.01%.

The nitro compound was reduced with iron and dilute hydrochloric acid. The amino-quinoline was distilled (b.p. 125° C. (1 mm.)) and recrystallized from ether to yield colorless prisms that melted at 97° C. Calc. for $C_{11}H_{12}N_2$: N, 16.28%. Found: N, 16.47, 16.46%.

The above 8-amino-4 : 5-dimethyl-quinoline was converted into 4 : 5-dimethyl-quinoline by the procedure already described for the elimination of the amino group from other 8-amino-quinolines. In this case, however, the reaction did not proceed in a very satisfactory manner. During the diazotization an insoluble brown substance was precipitated and this did not yield 4 : 5-dimethyl-quinoline on treatment with hypophosphorous acid. The distilled quinoline, obtained in 6% yield, crystallized readily on cooling. When recrystallized from hexane it melted at 71 to 72° C. and in admixture with the base obtained as described above there was no melting below 72° C. The picrate prepared from this melted at 230° C. either alone or in admixture with the above picrate.

For final purification the combined 4 : 5-dimethyl-quinoline from the two sources was recrystallized again from hexane. The colourless plates thus obtained melted sharply at 78° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 8.65%. The picrate was recrystallized twice more from acetone-methanol and it then melted at 233° C.

Acknowledgments

The authors are greatly indebted to Mr. Archie Ledingham and to Miss Frieda Hutt of these laboratories who carried out the numerous analyses with meticulous care, and to Mr. Marcel Chaput who prepared the 4 : 6-, the 4 : 7-, and the 4 : 8-dimethyl-quinolines and materially assisted in a number of syntheses involving the Skraup reaction.

References

1. ADAMS, R. and KORNBLUM, N. J. Am. Chem. Soc. 63(1) : 188-200. 1941.
2. BEREND, L. Ber. 17 : 1489-1490. 1884.
3. CLAISEN, L. Ber. 25 : 3164-3166. 1892.
4. CLARKE, H. T. and DAVIS, A. W. Org. Syntheses, 2 : 79-83. 1922.
5. COHN, E. W. J. Am. Chem. Soc. 52(9) : 3685-3688. 1930.
6. CROSSLEY, A. W. and RENOUF, N. J. Chem. Soc. 95 : 202-218. 1909.
7. DECKER, H. and REMFRY, P. Ber. 38 : 2773-2777. 1905.
8. DOEBNER, O. and MILLER, W. v. Ber. 16 : 2464-2472. 1883.
9. EWINS, A. J. and KING, H. J. Chem. Soc. 103 : 104-111. 1913.
10. FISCHER, O. Ber. 19 : 1036-1039. 1886.
11. GIRARDET, A. Helv. Chim. Acta, 14 : 513-515. 1931.
12. GREEN, A. G. and ROWE, F. M. J. Chem. Soc. 103 : 897-901. 1913.
13. KNORR, L. Ann. 236 : 69-115. 1886.
14. MAI, J. Ber. 35 : 162-163. 1902.
15. MARVEL, C. S. and HIERS, G. S. Org. Syntheses, 5: 71-74. 1925.
16. MIKHAILOV, G. I. J. Gen. Chem. (U.S.S.R.) 6 : 511-515. 1936. *Abstracted in* Chem. Abstracts, 30 : 6372. 1936.
17. MILLS, W. H., HARRIS, J. E. G., and LAMBOURNE, H. J. Chem. Soc. 119 : 1294-1300. 1921.
18. MORGAN, G. T. and HICKINBOTTOM, W. J. J. Soc. Chem. Ind. 45 : 221T-222T. 1926.
19. NOELTING, E., BRAUN, A., and THESMAR, G. Ber. 34 : 2242-2262. 1901.
20. PERKIN, W. H., JR. and ROBINSON, R. J. Chem. Soc. 105 : 2376-2392. 1914.
21. PFITZINGER, W. J. prakt. Chem. 66 : 263-264. 1902.
22. PLANT, S. G. P. and ROSSER, R. J. J. Chem. Soc. 1929 : 1861-1870. 1929.
23. PRILL, A. and WALTER, R. U.S. Pat. 1,806,563, May 19, 1931.
24. RIST, E. Ber. 23 : 3483-3487. 1890.
25. STAEDEL, W. and KOLB, A. Ann. 259 : 208-227. 1890.
26. TSEOU, H. F. Bull. soc. chim. Mém. (Sér. 5) 2 : 90-95. 1935.
27. ZEISEL, S. and DANIEK, M. Monatsh. 30 : 727-728. 1909.

THE ALKALOIDS OF *LYCOPODIUM* SPECIES

II. SOME DEGRADATION EXPERIMENTS WITH LYCOPODINE[1]

By Léo Marion[2] and Richard H. F. Manske[2]

Abstract

The dehydrogenation of lycopodine with selenium has yielded a mixture of five bases, two of which have been identified as 7-methyl-quinoline and 5 : 7-dimethyl-quinoline respectively. Heating the alkaloid with palladium on barium sulphate or with phthalic anhydride also yields 7-methyl-quinoline. It is concluded that the quinoline nucleus, completely hydrogenated, is present as such in lycopodine. The oxygen may be present as a cyclic ether.

The alkaloid lycopodine is the major basic constituent of a number of *Lycopodium* species now under investigation (2). Achmatowicz and Uzieblo (1) have assigned the formula $C_{16}H_{25}ON$ (which we have confirmed) to lycopodine and shown that methoxyl and N-methyl groups are absent as well as active hydrogen (Zerewetinoff). It is therefore probable that the nitrogen is common to two rings and that the oxygen is present either in a ketonic group or in a cyclic ether.

After treatment with phenyl-magnesium bromide at 100° C., lycopodine was recovered quantitatively. It could not be hydrogenated at 200° in butanol over Raney nickel at 2000 lb. per sq. in. These results seem to indicate that there is no ketonic group in lycopodine and that the oxygen is probably present in a cyclic ether linkage. Treatment of the alkaloid with hydrogen iodide and red phosphorus gave some confirmation of this supposition. There was obtained an amorphous base that contained iodine and slowly polymerized to an insoluble resin.

The dehydrogenation of the alkaloid with selenium yielded a complex mixture from which it was possible to isolate five bases as their picrates. Two of these have been identified as 7-methyl-quinoline and 5 : 7-dimethyl-quinoline respectively.

The formation of quinolines as the result of the high temperature decomposition of an alkaloid cannot be regarded as positive proof of the presence of the quinoline skeleton. The history of the chemistry of cytisine is ample warning that such assumptions may be premature. Nevertheless, 7-methyl-quinoline was obtained from lycopodine in two other ways, which from the nature of the reagents employed would not be expected to bring about the same change if this depended upon the opening and subsequent re-forming of rings. In the one experiment the alkaloid was heated in an atmosphere of nitrogen with palladium–barium-sulphate and in the other it was heated

---

[1] *Manuscript received March 17, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1062.

[2] *Chemist.*

with phthalic anhydride in an evacuated tube. It is therefore assumed that the quinoline nucleus, completely hydrogenated, is present as such in lycopodine.

Experimental

Degradation of Lycopodine with Selenium

Lycopodine (2 gm.) was mixed with black selenium (2 gm.) in a small flask carrying a column about 60 cm. long, at the top of which a side arm was connected to a downward condenser. A slow stream of nitrogen was kept sweeping into the flask through a capillary tube extending down the column. After the air had been displaced, the flask was dipped into a metal bath and, in the course of two hours, the temperature was raised gradually to 310° C. and kept at that temperature for one-half hour. Two more runs, each with 2 gm. of base, were made in exactly the same way.

The distillates were collected in ether and combined with the ether soluble portion obtained from the residues. The resulting ether solution was extracted repeatedly with small quantities of dilute hydrochloric acid, washed with water, and dried over sodium hydroxide. The ether was distilled off and the residual neutral oil (1.5 gm.) distilled *in vacuo*, b.p. 135 to 140° C. (2 mm.). This oil, although it contains no nitrogen, nevertheless gave a red colour with Ehrlich's reagent not unlike that given by indoles.

The residues from the selenium treatment which had been extracted with ether were repeatedly digested with methanol containing a little hydrochloric acid. The combined acid extracts were diluted with water, evaporated on the steam-bath to remove the methanol and the residue dissolved in water. After filtration through charcoal, the aqueous solution was combined with the acid extract obtained from the distillates.

Isolation of 7-Methyl-quinoline and 5 : 7-Dimethyl-quinoline

The combined acid solution was extracted with ether (discarded), basified, with strong sodium hydroxide and the precipitated base collected in ether. The ether solution was washed with water, dried over anhydrous potassium carbonate, and evaporated on the steam-bath. The residual dark oil (3 gm.) was fractionated *in vacuo*: fraction I, colourless oil, b.p. 80 to 90° C. (2 mm.); fraction II, colourless oil, b.p. 130 to 140° (2 mm.); fraction III, yellow oil, b.p. 170 to 180° (2 mm.); fraction IV, thick, light-brown oil, b.p. 185 to 210° (2 mm.); fraction V, an undistilled residue weighing a little less than half the combined distillates.

Fraction I was dissolved in methanol and added to a boiling solution of picric acid in methanol. The picrate, which separated in yellow needles, was recrystallized several times from methanol. The free base was regenerated, distilled (b.p. 75 to 80° C. (2 mm.), small end fractions being discarded), and reconverted to the picrate, m.p. 242°. Admixture with an authentic specimen of 7-methyl-quinoline picrate failed to depress the melting point. Calc. for $C_{16}H_{12}O_7N_4$: C, 51.69; H, 3.22; N, 15.05%. Found: C, 52.29; H, 3.62; N, 15.69%. The styphnate melted at 242° either alone or in admixture with an authentic specimen of 7-methyl-quinoline styphnate. The mother liquor of the first crystallization of 7-methyl-quinoline picrate was concentrated and, on cooling, it yielded a second, more soluble, picrate which, after one recrystallization, melted at 167°. Calc. for $C_{17}H_{18}O_7N_4$: C, 52.30; H, 4.62; N, 14.35%. Found: C, 52.15; H, 4.73; N, 14.69%.

Fraction II formed a picrate which, after several recrystallizations from acetone–methanol, melted at 246° C. and in admixture with 5 : 7-dimethyl-quinoline picrate melting at 249° (3) it melted at 248°. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.62; N, 14.51%. Found: C, 52.82; H, 3.83; N, 14.55%.

Fraction III also formed a picrate which, after two recrystallizations from boiling methanol, melted at 169° C. Calc. for $C_{22}H_{22}O_8N_4$: C, 56.17; H, 4.68; N, 11.91%. Found: C, 55.66; H, 4.60; N, 11.90%. The mother liquor from this picrate, when further concentrated yielded a more soluble picrate, m.p. 151°. Calc. for $C_{22}H_{24}O_7N_4$: C, 57.90; H, 5.26; N, 12.28%. Found: C, 58.01; H, 5.12; N, 12.83%.

Fraction IV, after refractionation, yielded an oil from which the same picrate (m.p. 169° C.) was obtained as from fraction III.

The undistilled residue (fraction V) was distilled under a pressure of 10^{-3} mm. but the various fractions obtained failed to yield crystalline picrates. There was present an appreciable amount of combined selenium in these fractions.

Dehydrogenation of Lycopodine

Lycopodine (about 0.5 gm.) was mixed with palladium–barium-sulphate (about 0.5 gm.) and the mixture heated in an oil bath in an atmosphere of nitrogen for seven hours at 250° C. The reaction mixture was allowed to cool and was distilled *in vacuo*. It yielded fraction I, colourless oil, b.p. 105 to 110° (1.5 mm.) and fraction II, thick, yellow oil, b.p. 130 to 150° (1.5 mm.).

Fraction I formed a picrate consisting of pale yellow needles, m.p. 242° C. Admixture with 7-methyl-quinoline picrate failed to depress the melting point. After concentration of the mother liquor there separated an oily picrate from which the base was liberated. This base yielded a crystalline perchlorate which, after repeated recrystallization from methanol, melted at 285°. This seems to be identical with the perchlorate obtained similarly from the product of the reaction of lycopodine with phthalic anhydride described below. The amount of material on hand, however, did not permit further comparison nor an analysis.

Reaction of Lycopodine with Phthalic Anhydride

Lycopodine (1 gm.) was mixed with phthalic anhydride (1 gm.), and the mixture was sealed into an evacuated tube and heated in an oil bath for seven hours at 250° C. The resulting black resin was repeatedly extracted with small quantities of hot dilute hydrochloric acid. The combined acid solution was filtered through charcoal, basified with strong sodium hydroxide, and extracted with ether. The ether solution was distilled on the steam-bath to remove the solvent and the residual oil fractionated *in vacuo*: fraction I, b.p. 100 to 110° (2 mm.) and fraction II, b.p. 130 to 145° (2 mm.). The first fraction yielded a picrate identified by melting point and mixed melting point as 7-methyl-quinoline picrate. The mother liquor from this picrate, when concentrated, deposited an oily picrate from which a base was liberated. This base formed a perchlorate crystallizable from methanol, m.p. 285°. Calc. for $C_{14}H_{23}N \cdot HClO_4$: C, 55.00; H, 7.86; N, 4.58%. Found: C, 54.81; H, 8.10; N, 4.35%.

References

1. ACHMATOWICZ, O. and UZIEBLO, W. Roczniki Chem. 18 : 88-95. 1938.
2. MANSKE, R. H. F. and MARION, L. Can. J. Research, B, 20(5) : 87-92. 1942.
3. MANSKE, R. H. F., MARION, L.; and LEGER, F. Can. J. Research, B, 20(7) : 133-152. 1942.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. B. AUGUST, 1942 NUMBER 8

THE ISOLATION OF CICUTIN FROM *CICUTA MACULATA* L.[1]

By Léo Marion[2]

Abstract

One of the constituents of the root of *Cicuta maculata* L. has been isolated in crystalline form. It has been found to contain three methoxyl groups and to possess a lactone structure.

The designation water hemlock has been applied indiscriminately to many species of the genus *Cicuta* (Umbelliferae) such as *C. vagans*, *C. occidentalis*, *C. virosa*, and *C. maculata*. The resinous, ether soluble products obtained from several of these plants have all been named cicutoxin, with the consequent implication that they are identical (1, 2, 4). It has long been known that a deadly poison is contained in the root of some species of *Cicuta* and that the resinous product possesses the toxic properties of the plant. *C. maculata* does not seem to have been investigated to the same extent as *C. occidentalis* or *C. virosa* although it is known to be poisonous. The toxicological studies, however, have yielded conflicting results, possibly because the species used was not always the same. Furthermore, the chemical knowledge extant, being based on experiments carried out with an amorphous material and not with a homogeneous substance, cannot be taken as definite.

Cicutoxin has been investigated chemically by Jacobson (2), by Schneider and Kotrba (5), and by Svagr (8). Jacobson, who isolated his cicutoxin from *C. occidentalis*, described it as a yellowish, viscous resin polymerizing spontaneously to a semisolid body of a ruby-red to reddish-brown colour. From an analysis of this resin Jacobson suggested the empirical formula $C_{19}H_{26}O_3$ for cicutoxin to which, on the basis of scanty evidence, he assigned a γ-pyrone structure.

In the course of the last twelve years, numerous complex coumarins have been isolated from various plants belonging to the Umbelliferae. It appeared, therefore, probable that the water hemlock might contain compounds possessing the coumarinic structure.

The root of *C. maculata* was extracted with petroleum ether and the extract, after separation of the fat and fatty acids, yielded a substance which could be crystallized from ether or methanol. In order to avoid ambiguity, it is

---

[1] *Manuscript received March 18, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1069.

[2] *Chemist.*

proposed to designate this substance by the name cicutin. Crystalline cicutin yielded analytical figures in good agreement with the empirical formula $C_{22}H_{22}O_7$, and it has been found to contain three methoxyl groups. It was found to be insoluble in aqueous sodium carbonate, but soluble in sodium hydroxide. When treated with sodium hydroxide and dimethyl sulphate it gave rise to an ester-ether which, on saponification, produced an acid containing four methoxyl groups. Diazomethane, however, failed to react. Furthermore, when cicutin was dissolved in standard sodium hydroxide and the solution titrated with standard hydrochloric acid, a potentiometric curve (Fig. 1) was obtained which exhibits two horizontal sections, each corresponding to a group in the molecule which combined with sodium hydroxide. The foregoing facts indicate a lactone structure. Of the seven atoms of oxygen present in cicutin, five are accounted for by the three methoxyl groups and the lactone ring. Neither of the two remaining oxygen atoms seems to be part of a furan ring since all attempts to oxidize cicutin with hydrogen peroxide according to the procedure used by Späth and v. Christiani (6) have so far failed to produce furan-2 : 3-dicarboxylic acid. Further than this, no insight into the constitution of cicutin has been obtained.

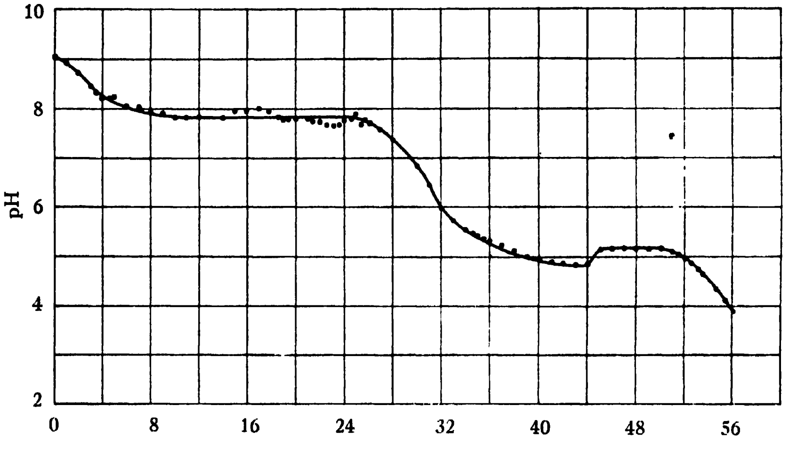


FIG. 1.

Dr. C. A. Morrell, pharmacologist of the Department of Pensions and National Health, Ottawa, kindly undertook to determine the toxicity of the crude extract and of pure cicutin, and the author takes this opportunity to acknowledge his indebtedness. The residue from the petroleum ether extract of the root, dissolved in 20% alcohol, was found to be toxic to frogs and to cause the same symptoms as described by earlier investigators (3). No toxicity, however, was observed towards guinea pigs. Unfortunately, it was not possible to determine whether the same toxicity could be attributed to crystalline cicutin, owing to its insolubility in dilute alcohol or in any of the suitable solvents.

Experimental

Isolation of Cicutin

The plant material utilized for this work was collected in the vicinity of Ottawa and kindly identified by Dr. H. Senn, Botanist at the Dominion Experimental Farm, Ottawa, as *Cicuta maculata* L. The cleaned roots, air-dried and ground, weighed 11.4 kilos. They were extracted in Soxhlets with petroleum ether and the solvent was removed by distillation from the combined extracts. After standing for several days, the oily residue had deposited a crystalline solid which was filtered (Filtrate *A*) through a fritted glass funnel. The crystalline solid was dissolved in methanol (200 cc.), added to a solution of sodium hydroxide (40 gm.) in methanol (200 cc.), and allowed to stand at room temperature for five hours, with frequent shaking. At the conclusion of this treatment, the methanol was distilled under reduced pressure, water (2 litres) added to the residue, the mixture stirred, and allowed to stand overnight. Next day a sludge had settled to the bottom, and the clear supernatant liquor was siphoned off and filtered through a layer of Celite. Water was added to the sludge, which was stirred and allowed to settle, and the supernatant liquor was siphoned off, and filtered. The combined filtrates were acidified with hydrochloric acid, allowed to stand several hours, and extracted repeatedly with ether. During this extraction, a crystalline solid separated which was filtered off, washed with ether, and recrystallized repeatedly from methanol. It was obtained finally as soft colourless needles, m.p. 171°.*

The combined ether extracts still contained free fatty acids, and in order to remove these the ether solution was placed in a separatory funnel and 0.5% aqueous sodium hydroxide (2 litres) was run, drop by drop, into the funnel, the aqueous layer being drawn off from time to time. The ether layer was afterwards washed with water, dried over sodium chloride, and distilled. A crystalline residue weighing 17 gm. was left, which when recrystallized from a mixture of methanol and ether melted at 168° C. After several recrystallizations from methanol, it separated as soft needles, m.p. 171°, identical with the substance obtained above. Calc. for $C_{22}H_{22}O_7$: C, 66.33; H, 5.53; 3 OCH_3, 23.36%; mol. wt. 398. Found: C, 66.29, 66.49; H, 5.45, 5.49; OCH_3, 23.22, 23.34%; mol. wt. (Rast), 358, 384.

The oily filtrate *A*, mentioned above, was dissolved in methanol (200 cc.), poured into a solution of sodium hydroxide (40 gm.) in methanol (200 cc.), and treated exactly as described in the case of the solid material. This yielded a further small quantity of cicutin. The total yield of purified cicutin amounted to 0.13% of the weight of the dried roots.

---

* *All melting points are corrected.*

Hydrolytic Methylation of Cicutin

Following the procedure described by Späth, Dey, and Tyray (7), cicutin (150 mg.) was dissolved in 3% aqueous sodium hydroxide (20 cc.) with the aid of heat. To this solution was added 10% sodium hydroxide (12.4 cc.) and freshly distilled dimethyl sulphate (3.3 cc.), and the mixture boiled under reflux for seven minutes. This treatment was repeated four times, the same quantities of 10% sodium hydroxide and dimethyl sulphate being added between the periods of heating. After the fifth heating, 10% aqueous sodium hydroxide (10 cc.) was added and the flask kept on the steam-bath for 10 min. to saponify the ester. The solution was cooled, acidified with 6*N* hydrochloric acid (10 cc.) and allowed to stand overnight. The white precipitate was collected in ether, extracted with three portions of 3% aqueous sodium bicarbonate (15 cc. each), washed with water, and dried over sodium chloride. Removal of the ether by distillation left a small residue of unchanged cicutin; m.p. 170° C. either alone or in admixture with an authentic sample. The combined sodium bicarbonate extracts were acidified with dilute (1 : 1) hydrochloric acid and the precipitated acid was collected in ether. The ethereal solution was washed with water, dried, and distilled to remove the solvent. The residue consisted of a crystalline acid which, after recrystallization from boiling methanol, melted at 194 to 195°. Yield, 80 mg. Calc. for $C_{23}H_{26}O_8$: 4 OCH_3 , 28.84%. Found: OCH_3 , 27.04%.

Potentiometric Titration of Cicutin

Cicutin (0.1096 gm.) was dissolved in 0.0092 *N* sodium hydroxide (60.0 cc.), the solution kept well stirred and 0.0108 *N* hydrochloric acid added in small quantities at a time. After each addition the equilibrium value of the pH was read on a Beckman pH meter. The results are plotted in Fig. 1. The distance along the abscissa from the origin of the first plateau to the end of the second corresponds to a quantity of sodium hydroxide equivalent to a molecular weight of 419 for cicutin. The molecular weight calculated for $C_{22}H_{22}O_7$ is 398.

References

1. Boehm, R. Arch. exptl. Path. Pharmakol. 5 : 279. 1876.
2. Jacobson, C. A. J. Am. Chem. Soc. 37(4) : 916-934. 1915.
3. Jacobson, C. A. Nevada Agr. Expt. Sta. Bull. 81. 1915.
4. Pohl, J. Arch. exptl. Path. Pharmakol. 34 : 258-267. 1884.
5. Schneider, J. Z. and Kotrba, J. Chem. Abstracts, 26(12) : 3280. 1932.
6. Späth, E. and Christiani, A. F. v. Ber. 66 : 1150-1156. 1933.
7. Späth, E., Dey, B. B., and Tyray, E. Ber. 72 : 53-56. 1939.
8. Svagr, E. Chem. Listy, 25 : 257-260. 1931.

STUDIES ON DICYANOTRIAZOLE

I. THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF DICYANOTRIAZOLE AT 25° C.[1]

By E. G. Taylor[2]

Abstract

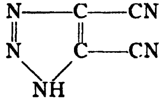
Previous experimental studies of dicyanotriazole have resulted in statements that the compound is an acid comparable in strength with the strong mineral acids.

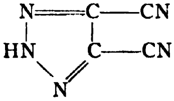
In the present work, measurements of the equivalent conductance of dicyanotriazole in dilute aqueous solution give the dissociation constant of the acid as 3.378×10^{-2} at 25° C., thus showing it to be an acid possessing about the same strength as dichloracetic acid.

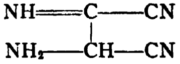
The limiting equivalent conductance of dicyanotriazole at 25° C. is 384.9. The earlier work gave a value of 397.44.

Introduction

In this laboratory a comprehensive investigation of the properties of dicyanotriazole has been undertaken. This substance was first obtained by Grishkevich-Trokhimovskii (6). Fialkoff (3) confirmed Trokhimovskii's observation that the dicyanotriazole existed in two crystalline modifications—a yellow form and a colourless form. The colourless form, to which Formula I was given, was obtained by sublimation of the yellow form (Formula II)


(I)


(II)


(III)

Hinkel and his co-workers (7) have shown that the yellow variety is merely an impure form of dicyanotriazole. These observations have been confirmed in the present work.

Fialkoff (3) states that dicyanotriazole is to be regarded as a strong acid comparable in strength with hydrochloric or nitric acid, but the published data do not permit an accurate calculation of the dissociation constant of the acid. In his paper he reports measurements of the electrical conductances of the supposed two varieties. The difference in the reported values is small (3 to 4%), and it becomes inappreciable at the higher concentrations investigated.

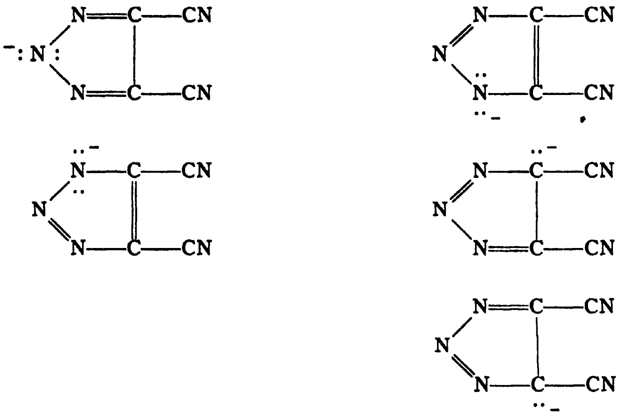
Using the results of conductance measurements on the sodium salt of dicyanotriazole, Fialkoff arrives at a Λ_0 value of 98.64 for this salt. Subtracting the mobility of the sodium ion, i.e., 51.2 at 25° C. (10), gives the mobility of the dicyanotriazole anion as 47.44. Finally taking the mobility of the hydrogen ion as 350 he gives the Λ_0 value for dicyanotriazole as 397.44. Using this value of the limiting conductance, Fialkoff calculates the conductance ratios over the concentration range 0.002 to 0.4 N. These values vary from 0.87 in the dilute solutions to 0.25 in concentrated solution. It seems clear that dicyanotriazole is highly dissociated in dilute aqueous solution—much more so than most organic acids.

---

[1] *Manuscript received March 28, 1942.*
Contribution from the Chemical Laboratories, Queen's University, Kingston, Ont.

[2] *Lecturer in Chemistry.*

A study of the formula of dicyanotriazole reveals an interesting situation. The anion formed by ionization of the dicyanotriazole exhibits lack of saturation of the atomic valencies. To explain the apparent stability of the anion of dicyanotriazole, the concept of quantum mechanical resonance must be used. The anion resonates among the following five structures:



and hence the molecule is made unstable relative to the anion. In addition the ionic character of the triple bond of the cyanide group (13, p. 184) assists in stabilizing the structure of the anion. It is clear therefore that dicyanotriazole may be a relatively strong acid, particularly in aqueous solution.

In this paper, measurements of the conductance of dicyanotriazole in aqueous solution at 25° C. over the concentration range 2×10^{-4} to 8×10^{-3} N are reported. An accurate value of the dissociation constant has been calculated and the mobility of the anion of dicyanotriazole obtained.

Experimental

Apparatus

Conductance measurements were made with an accurate a-c. direct reading type of bridge built in accordance with modern specifications. A variable frequency oscillator (600 to 3000 cycles) provided the alternating current while a pair of telephones in conjunction with a simple pentode amplifier served as detector. The conductance cell was of the Erlenmeyer type described by Cox, Kraus, and Fuoss (1). The electrodes were lightly platinized. The cell constant was 1.280—determined by intercomparison with a cell the constant of which was 4.873. The constant of the latter cell was determined using Jones and Bradshaw's data (8) for 0.01 demal potassium chloride solution at 25° C. The cell capacitance was negligible and measurements of resistances were made at 600, 1000, and 2000 cycles. Polarization corrections were applied when necessary (9). An oil thermostat controlled by a thyratron tube maintained a temperature of 25.00° C. (± 0.02° C.).

Materials

Conductance water was prepared by fractional condensation of steam in an all-Pyrex still in a current of air freed from carbon dioxide and ammonia.

Preparation of Dicyanotriazole

Pure hydrogen cyanide was prepared by the usual method of dropping saturated sodium cyanide solution into 50% sulphuric acid solution heated to 80° C. The liquid hydrogen cyanide was dried by shaking with anhydrous sodium sulphate. To the dried liquid about 3% of its weight of sodium cyanide was added. On standing for 24 to 48 hr. in a closed vessel the whole mass underwent a violent reaction, resulting in the production of a black coal-like mass.

The black material was extracted with ether in a Soxhlet apparatus. The ether solution on evaporation yielded a dark brown crystalline substance, which has been shown to be iminoaminosuccinonitrile (7), Formula III. The yield was about 3%, based on the hydrogen cyanide used.

The crude brown product was suspended in water and diazotized with sodium nitrite solution and hydrochloric acid. After careful diazotization at a temperature below 10° C. the solution was heated to 90° on a steam-bath and treated with Norit. The mixture was then filtered and the cold colourless filtrate extracted several times with ether. On evaporation of the ether, white crystalline dicyanotriazole remained (7). The dicyanotriazole was crystallized repeatedly from ethylene dichloride and finally dried over phosphorus pentoxide *in vacuo*. As a test of its purity, conductance measurements were made with samples that had been crystallized different numbers of times. Agreement between the electrical measurements is an excellent criterion of purity. The melting point of the dicyanotriazole was 148° C. (corrected).

Method

All solutions were made up by a weight dilution method (11). About 100 mg. of the acid was weighed out into the conductance cell and about 150 gm. of conductance water weighed into the cell. The cell was placed in the thermostat and the resistance measured when temperature equilibrium was attained. The cell was then removed from the thermostat, wiped clean of oil, and about half the solution removed by means of an evacuated weight pipette provided with a long capillary tip. The solution removed was replaced by conductance water and after weighing again another resistance measurement was made. This procedure was repeated five or six times for each run.

In all cases the measured resistances were perfectly constant and did not vary with time, even over long periods.

Volume concentrations were calculated on the assumption that the densities of the solution were the same as the density of the pure solvent. No correction was made for the conductance of the water.

Results

The experimental results are summarized in Table I. Three independent runs were carried out. A plot of Λ against $\sqrt{c}$ is shown in Fig. 1.

TABLE I

THE CONDUCTANCE OF DICYANOTRIAZOLE IN WATER AT 25° C.

Concentration, $c \times 10^4$	Equivalent conductance, Λ	Concentration, $c \times 10^4$	Equivalent conductance, Λ
(a) Specific conductance of water = 8×10^{-7} *r.o.*			
82.85	317.7	9.215	371.2
50.42	336.2	4.175	376.6
31.70	349.8	2.056	377.2
19.54	360.7		
(b) Specific conductance of water = 1.0×10^{-6} *r.o.*			
47.50	338.8	6.901	373.8
27.17	354.2	2.871	377.0
12.82	367.6		
(c) Specific conductance of water = 1.0×10^{-6} *r.o.*			
58.49	331.2	11.18	368.7
29.32	352.2	4.665	375.3
18.70	361.3	2.100	375.8

Discussion

It is impossible to obtain the Λ_0 value for dicyanotriazole by extrapolation of the $\Lambda/\sqrt{c}$ plot, since its slope is considerably greater than that predicted by the Onsager equation (12). Furthermore, the Λ values are not reliable at concentrations less than 4×10^{-4} N, probably because of a reaction between impurities in the water and the dicyanotriazole.

To obtain the Λ_0 value and the true thermodynamic dissociation constant of dicyanotriazole, recourse is made to the limiting laws that have been developed on the basis of Coulombic interaction between the ions. These are the following:

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}), \quad (5)$$

where γ satisfies the ordinary mass law equation

$$\frac{c\gamma^2 f^2}{1 - \gamma} = K,$$

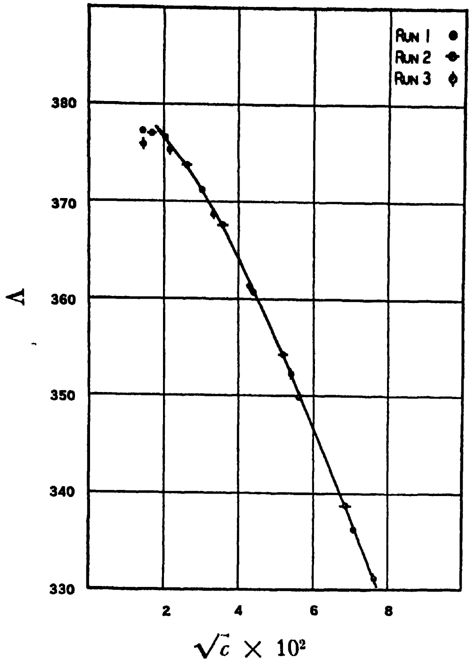


FIG. 1. *Conductance curve of dicyanotriazole in water at 25° C.*

and f is given by the Debye–Hückel limiting equation (2)

$$-\log f = \beta\sqrt{c\gamma},$$

Λ = equivalent conductance at concentration C (gram-equivalents per litre of solution),
Λ_0 = limiting conductance,
γ = fraction of solute dissociated,
f = activity coefficient,
α = Onsager's coefficient (12),
β = Debye and Hückels' constant,
K = dissociation constant.

Fuoss (4) has introduced a function $F(z)$, where $z = \alpha\Lambda_0^{-\frac{3}{2}}\sqrt{c\Lambda}$, thereby obtaining the relation between equivalent conductance and concentration in the form of a straight line. This final equation is

$$\frac{F(z)}{\Lambda} = \frac{1}{K\Lambda_0^2}\,\frac{C\Lambda f^2}{F(z)} + \frac{1}{\Lambda_0}\,.$$

The values of $\frac{F(z)}{\Lambda}$ and $\frac{c\Lambda f^2}{F(z)}$ for dicyanotriazole are given in Table II. The third column of Table II gives the percentage deviation

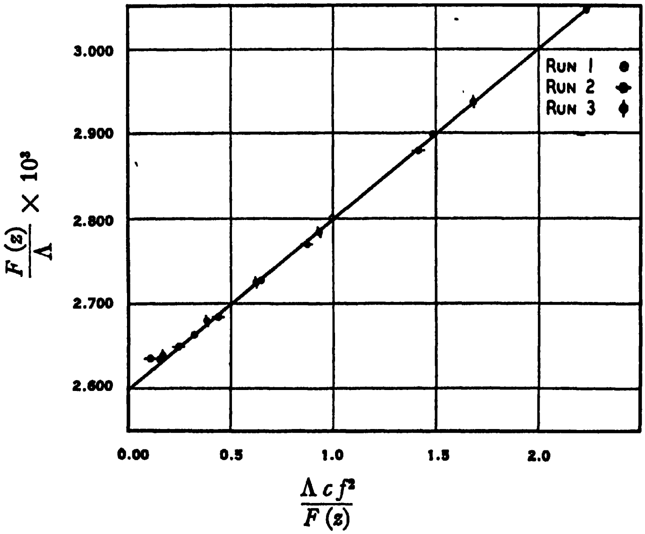
$$\Delta = \left\{\left(\frac{F(z)}{\Lambda}\right)_{\text{interpol.}} - \left(\frac{F(z)}{\Lambda}\right)_{\text{obs.}}\right\} 100 \left(\frac{\Lambda}{F(z)}\right)_{\text{interpol.}}$$

when a straight line is drawn through the experimental points. When the deviation is positive $\Lambda_{obs.} > \Lambda_{interpol.}$ Fig. 2 shows the straight line relation between $\frac{c\Lambda f^2}{F(z)}$ and $\frac{F(z)}{\Lambda}$.

TABLE II

CALCULATED VALUES OF $\frac{F(z)}{\Lambda}$ AND $\frac{c\Lambda f^2}{F(z)}$ FOR DICYANOTRIAZOLE IN WATER AT 25° C.

	$\frac{c\Lambda f^2}{F(z)}$	$\frac{F(z)}{\Lambda} \times 10^3$	Δ
(*a*)	2.237	3.045	−0.00
	1.487	2.898	−0.10
	0.9979	2.800	−0.09
	0.6479	2.727	−0.00
	0.3227	2.663	−0.00
	0.1511	2.634	−0.14
(*b*)	1.417	2.878	+0.09
	0.8724	2.769	+0.11
	0.4400	2.683	+0.11
	0.2452	2.649	−0.09
	0.1048	2.635	−0.57
(*c*)	1.685	2.936	−0.07
	0.9326	2.783	+0.05
	0.6222	2.724	−0.04
	0.3866	2.678	−0.15
	0.1682	2.638	−0.23



Test of the Fuoss conductance function for dicyanotriazole in water at 25° C.

The agreement with the linear relation is seen to be good, except for one or two points for very dilute solutions. The intercept of the straight line on the $\frac{F(z)}{\Lambda}$ axis is 0.002598, giving a value of 384.9 for Λ_0. The slope of the line, equal to $\frac{1}{K\Lambda_0^2}$, is 0.0001998, which yields a value of 3.378×10^{-2} for the dissociation constant of dicyanotriazole.

The mobility of the hydrogen ion at 25° C. is 349.72 (10), and therefore the mobility of the dicyanotriazole anion is 35.2.

It appears that dicyanotriazole is a relatively strong acid comparable in strength with dichloracetic acid for which $K = 5.14 \times 10^{-2}$. It is interesting that the value for the anion mobility is close to that for the propionate anion—34.3—which contains 10 atoms compared with 9 for the dicyanotriazole anion. The value obtained by Fialkoff—47.44 (3)—appears much too high for an anion of this nature.

Acknowledgment

Thanks are due to the Science Research Committee of Queen's University for financial assistance in purchasing apparatus and for providing the assistance of Mr. A. H. Haley, who carried out the lengthy preparation of the tetrapolymer of hydrogen cyanide.

References

1. Cox, N. L., Kraus, C. A., and Fuoss, R. M. Trans. Faraday Soc. 31 : 749-761. 1935.
2. Debye, P. and Hückel, E. Physik. Z. 24(9) : 185-206. 1923.
3. Fialkoff, J. A. Bull soc. chim. (Sér. 4) 41 : 1209-1217. 1927.
4. Fuoss, R. M. J. Am. Chem. Soc. 57(3) : 488-489. 1935.
5. Fuoss, R. M. and Kraus, C. A. J. Am. Chem. Soc. 55(2) : 476-488. 1933.
6. Grishkevich-Trokhimovskii, E. J. soc. phys.-chim. russe, 55 : 548-550. 1924. (See Chem. Abstracts, 19(18) : 2810. 1925.)
7. Hinkel, L. E., Richards, G. O., and Thomas, O. J. Chem. Soc. 1937 : 1432-1437. 1937.
8. Jones, G. and Bradshaw, B. C. J. Am. Chem. Soc. 55(5) : 1780-1800. 1933.
9. Jones, G. and Christian, S. M. J. Am. Chem. Soc. 57(2) : 272-280. 1935.
10. MacInnes, D. A., Shedlovsky, T., and Longsworth, L. G. J. Am. Chem. Soc. 54(7) : 2758-2762. 1932.
11. Mead, D. J., Fuoss, R. M., and Kraus, C. A. Trans. Faraday Soc. 32 : 594-606. 1936.
12. Onsager, L. Physik. Z. 28(8) : 277-298. 1927.
13. Pauling, L. C. Nature of the chemical bond. Cornell University Press, Ithaca, N.Y. 1939.

THE HYDROLYSIS OF PROPIONITRILE IN CONCENTRATED SOLUTIONS OF MINERAL ACIDS[1]

BY J. D. MCLEAN[2], B. S. RABINOVITCH[3], AND C. A. WINKLER[4]

Abstract

The study of the hydrolysis of propionitrile in concentrated acid solutions has been extended to hydrobromic, nitric, and sulphuric acids for a range of acid concentrations. For the system of irreversible, unimolecular consecutive reactions, nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid, $k_1 \ll k_2$ for all acid concentrations below 4 N. At higher concentrations, k_1 and k_2 are of the same order, and, in the case of sulphuric acid, k_1 becomes $\gg k_2$ at concentrations above 20 N. The observed activation energy decreases with increasing acid concentration for all acids. The specific differences in rate increase with acid concentration may be accounted for by the specific variations of A and E for each acid.

Introduction

In a previous investigation (4) of the hydrolysis of propionitrile in hydrochloric acid solutions from 0.5 to 10 N, it was shown that the system, nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid, provides an example of unimolecular irreversible consecutive reactions over the complete range $k_1 \ll k_2$ (less than 4 N) to $k_1 \gg k_2$ (estimated above 11 N). This behaviour is contrary to a recent report (3) on the subject. A large decrease in activation energy of 6.7 Cal. over the range 1 to 10 N accounted in large measure for the marked increase in rate with acid concentration.

It was of interest to ascertain if the behaviour observed with hydrochloric is typical for mineral acids, and the investigation has therefore been extended to include sulphuric, nitric, and hydrobromic acids. At the same time, the parameters of the Arrhenius equation have been evaluated for each acid, over a range of concentrations, in a further effort to assess the importance of these factors for reactions in concentrated media.

Materials and Procedure

The acid solutions were prepared by dilution of reagent grade acids, standardized by both density and titration measurements.

Purification of propionitrile and preparation of its solutions were carried out as described previously (4).

Temperature was regulated to within 0.1° C., and measured with standard thermometers.

Krieble and Noll (3) have indicated that for sulphuric and hydrobromic acids, at concentrations comparable with those employed here, the hydrolysis

---

[1] *Manuscript received in original form February 4, 1942, and as revised, April 25, 1942. Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.*

[2] *Demonstrator in Chemistry.*

[3] *Holder of a Studentship under the National Research Council of Canada.*

[4] *Assistant Professor of Chemistry.*

of simple aliphatic nitriles may be followed by estimation of ammonia, i.e., that hydrolysis of the intermediate amide proceeds at a much faster rate than that of nitrile. The results of the previous study with hydrochloric acid suggested, however, that at higher acid concentrations both ammonia and amide should be determined. In the present study, ammonia alone, and the total of amide and ammonia both have been determined to evaluate the relative velocities of the two consecutive reactions and the influence of the intermediate on the over-all rate. The analytical procedures were the same as for hydrochloric acid.

Results

Experimental conditions and velocity constants for each of the three acids are shown in Tables I and II. The limited number of acid concentrations employed is sufficient to show the trends of the reaction rates. It may be seen that for acid concentrations of 1 to 4 *N*, the rate of amide hydrolysis is much greater (k amide: k nitrile $>$ 100 : 1) than that of the nitrile, for all acids. This is evident from the equivalence of the k values obtained for hydrobromic acid by the two analytical methods, and also from the good constants obtained for nitric and sulphuric acids where analysis for ammonia only was made. Thus, determination of ammonia alone is sufficient at the more dilute concentrations. At higher acid concentrations, analysis for ammonia indicates that the hydrolysis has an induction period, which is eliminated, however, when data for both amide and ammonia content are considered. At these concentrations, therefore, the rates of nitrile and amide hydrolysis are of the same order.

The relations between the nature of the induction periods and the relative rates of the consecutive reactions of nitrile and amide have been previously discussed in the work on hydrochloric acid. For hydrobromic acid at 7.68 *N*, the velocity of hydrolysis, as given by ammonia formation, approaches the true nitrile value. However, the induction period is very pronounced and the ratio, k amide: k nitrile, is therefore less than 10 : 1, and is probably about 3 : 1. Since the upper limit of hydrobromic acid concentration ordinarily available is restricted, the rate ratios of the two reactions in hydrobromic acid solutions apparently may vary from k (nitrile) $\ll$ k (amide) (less than 4 *N*) to k (nitrile) $\backsim$ k (amide) (about 8 *N*).

With 13.01 *N* nitric acid, the k values obtained by analysis for ammonia do not approach the true nitrile rate, but level off at a much lower value which corresponds to the rate of amide hydrolysis, as the work with hydrochloric acid has shown. The ratio of k (nitrile) : k (amide) is evidently about 3 : 1, corresponding to an induction period of the observed magnitude. It is evident that for nitric acid concentrations commonly available, the above rate ratio varies from less than 1 : 100 (less than 4 *N*) to approximately 15 : 1 (estimated for 15 *N*).

The data for sulphuric acid indicate that at 10.60 *N* the ratio of the velocities of nitrile and amide hydrolysis is about 1 : 30. At 18.86 *N* the ratio is about 10 : 1 and determination of ammonia only leads to the evaluation

TABLE I

DATA ON THE NATURE OF CONSECUTIVE REACTIONS OF NITRILE AND AMIDE FOR THE DIFFERENT ACIDS

Acid	Acid concn., normality	A—Analysed for ammonia. AA—Analysed for ammonia + amide.	Temp., ° C.	$k \times 10^3$ hr.$^{-1}$						
				% NH_3*						
				10-20	20-30	30-40	40-50	50-60	60-70	70-80
HBr	1.00**	A	86.5	0.996	0.964		0.942	0.931		
		AA	86.7	1.02	0.992	0.940	0.927	0.923	0.906	
	4.00	A	107.4	75.0	73.8		73.2	73.2		70.2
		AA	107.4	73.8	75.6	75.6	73.0	73.1	72.6	
	7.68	A	68.1	12.7	15.8	18.1		22.9	23.9	26.9
		AA	68.1	27.1	28.0	27.3	28.3	26.4		
HNO₃	1.00**	A	113.6	12.8 13.0	12.5		12.2	12.1		
	4.00	A	107.4		72.0 73.8		75.0	74.1 74.4	73.2	73.6
	13.01	A	80.5	12.0	18.2	20.6	22.5 23.0	23.7		
		AA	80.5	88.2	92.9	91.0	88.4	87.2	92.6	
H_2SO_4	2.00**	A	86.5	1.16	1.12 1.13	1.13	1.10			
	10.60	A	80.6	17.1	18.8	19.3	19.5	19.8	20.7	
		AA	80.6	20.5	20.7	20.6	20.2	21.2	20.9	21.1 19.8
	18.86	A	79.5	21.1	27.4 29.8		32.4	34.6		
		AA	68.1	93.6	93.7	95.4	95.6	93.5	95.5	93.2

* *Refers to runs analysed for ammonia only; given to indicate region where k was found.*

** *At these lower concentrations, depletion of the catalyst, by ammonia formation, causes a downward drift in the unimolecular velocity constants as the reaction progresses; the bimolecular values are quite satisfactory.*

of *k* for propionamide. Since the nitrile velocity continues to increase, while that of the amide decreases quite markedly (2) with increased acid concentrations, it appears that the hydrolysis in sulphuric acid covers the whole range *k* (propionitrile) $\ll$ *k* (propionamide) (2 *N*) to *k* (nitrile) $\gg$ *k* (amide) (estimated above 20 *N*). Karve and Gharpure (1) have investigated the hydrolysis of aliphatic nitriles in glacial-acetic–concentrated-sulphuric-acid medium over a range of sulphuric acid concentrations from 16.34 to 26.21 *N*. They found that only a small amount of amide was isolable in the reaction mixture. This behaviour differs from that observed here, probably because their experimental conditions were different. The validity of the conclusions drawn here are supported by the fact that aliphatic nitriles, dissolved in 96% sulphuric acid, give rise almost quantitatively to the amide which can then be isolated (5, p. 139).

The unimolecular rate constants for each acid over a range of concentrations and temperatures are given in Table II. The average deviation from the mean in a given run was about 1 to 3%. No corrections have been applied

TABLE II

RATE CONSTANTS FOR PROPIONITRILE HYDROLYSIS AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURES

Acid	Acid normality	Nitrile normality	Temp., ° C.	$k \times 10^2$ hr.$^{-1}$
Hydrobromic acid	1.00	0.4040	86.7	1.02
			100.4	3.80
			113.6	12.1
			124.8	31.2
	4.00	0.4063	78.7	4.58
			89.6	13.0
			100.7	37.5
			107.4	73.4
			109.6	84.9
	7.68	0.1638	48.7	3.65
			60.5	12.8
			68.1	27.4
			79.7	80.1
Nitric acid	1.00	0.4040	86.5	0.936
			100.4	3.81
			113.6	12.8
			124.8	33.1
	4.00	0.4067	78.7	4.66
			89.6	13.2
			100.4	38.8
			107.4	73.8
	13.01	0.2593	48.7	4.89
			60.5	15.1
			68.1	29.9
			80.5	90.0
Sulphuric acid	2.00	0.4057	86.5	1.15
			100.4	4.26
			113.6	14.2
			125.3	36.9
	10.60	0.5244	58.5	2.07
			69.9	7.09
			80.6	20.6
			92.4	66.0
	18.86	0.3883	48.7	12.3
			60.5	42.2
			64.6	66.8
			68.1	94.3

in this work for concentrations taken as at 25° C., or for the variation of collision number with temperature; for comparative purposes these errors should largely cancel. The Arrhenius lines were constructed from the data,* and the values of E calculated. These, together with the corresponding values of A, are given in Table III, which also includes the previous results with hydrochloric acid for purposes of comparison. In calculating the A factor, the velocity constants have been expressed in seconds, and these values have been divided by the molarity of the acid to reduce the solutions to unit acid concentration, where sulphuric acid is considered to function as a monobasic acid. Although this procedure is a step in the right direction, it is of necessity arbitrary, particularly in the case of sulphuric acid, and may cause apparent deviation from a general shift in A (e.g., 1 and 4 N hydrobromic acid).

TABLE III

THE ARRHENIUS CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE AT VARIOUS CONCENTRATIONS OF MINERAL ACIDS

Acid	Acid concentration, N	$\log_{10} A$	E, cal.
HBr	1.00	10.1	25,700
	4.00	10.2	25,300
	7.68	9.5	22,600
HNO_3	1.00	10.7	26,700
	4.00	10.7	26,100
	13.01	8.1	20,700
H_2SO_4	2.00	10.1	25,700
	10.60	10.1	24,400
	18.86	10.2	23,000
HCl	1.00	10.04	25,600
	4.00	9.95	24,800
	5.02	9.68	23,900
	6.48	8.92	21,800
	8.47	8.85	20,100
	10.13	8.78	18,900

It is seen from Table III that at the more dilute acid concentrations the activation energies are substantially the same. At higher concentrations, however, specific differences appear and considerable variation in activation energies at comparable concentrations is found.

The variation of rate with acid concentration at a given temperature is shown in Table IV, which also includes earlier data for hydrochloric acid. Velocities have been obtained from the Arrhenius lines. The relative rates for different acids at comparable concentrations will, of course, vary with temperature, particularly at high acid concentrations where the activation energies differ very appreciably.

It is evident that at lower concentrations the velocities are essentially the same. At higher concentrations, however, specific differences in rate become

TABLE IV

DATA FOR THE VARIATION OF RATE OF HYDROLYSIS WITH ACID CONCENTRATION FOR DIFFERENT ACIDS (87.2° C.)

Acid	$k \times 10^2$ hr.$^{-1}$					
	Acid molarity					
	1.00	4.00	5.02**–5.30†	6.48**–7.68*	8.48**–9.43†	13.01
HBr	1.14	11.4		157		
HNO_3	1.01	11.5				153
H_2SO_4	1.22		39.8		567	
HCl	1.14	12.1	28.5	120	1200	

** *HCl.* * *HBr.* † *H_2SO_4.*

evident, hydrochloric acid being the most efficient, followed by sulphuric, hydrobromic, and nitric acids in the order named. This behaviour has been noted previously (3), except for nitric acid.

The specific differences in rate increase with acid concentration may be accounted for by the specific variations of A and E. The reality of such changes in A and E for nitrile hydrolysis have been discussed previously (4). With sulphuric acid, the increase in rate with acid concentration follows the decrease in activation energy, but both the rate increase with acid concentration and the decrease in E are less marked than with hydrochloric acid. With hydrobromic acid, the value of A decreases at a concentration of 7.68 N, but the decrease in E is dominant and largely governs the rate. With nitric acid, a marked decrease in the value of A was observed at 13.01 N. The rate increase, therefore, is much slower than is indicated by the decrease in E.

It has thus been shown that in the acid catalyzed hydrolysis of propionitrile, the previously observed decrease in activation energy with increase of hydrochloric acid concentration is typical for mineral acids. As might be expected, the magnitude of the shift here is specific. Variation of an acid component of the critical complex would alter the characteristics of that intermediate. In addition, the general characteristics of the acid media at high acid concentrations are quite different and will result in specificity of the interaction between reactants, complex and medium.

References

1. KARVE, D. and GHARPURE, D. V. J. Univ. Bombay, 8 (Pt. 3) : 139-159. 1939.
2. KRIEBLE, V. K. and HOLST, K. A. J. Am. Chem. Soc. 60 (12) : 2976-2980. 1938.
3. KRIEBLE, V. K. and NOLL, C. I. J. Am. Chem. Soc. 61 (3) : 560-563. 1939.
4. RABINOVITCH, B. S., WINKLER, C. A., and STEWART, A. R. P. Can. J. Research, B, 20 (7) : 121-132. 1942.
5. SIDGWICK, N. V. The organic chemistry of nitrogen. New ed. Oxford University Press, London. 1937.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. SEPTEMBER, 1942 NUMBER 9

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXVII. SYNTHESIS OF METHYLATED GLUCOSE DERIVATIVES[1]

BY TAYLOR H. EVANS[2], IRVING LEVI[3], W. LINCOLN HAWKINS[4], AND HAROLD HIBBERT[5]

Abstract

The Haworth methylation technique has been modified to provide improved methods of synthesis of 2,3-dimethyl-α- and β-methyl glucosides and 2,3,4,6-tetramethyl glucose from glucose, and of 2,3,4-trimethyl methyl glucosides from levoglucosan. A new crystalline derivative of 2,3-dimethyl glucose, the gluconophenylhydrazide, has been prepared and found to serve as a valuable identification medium.

Introduction

Various derivatives of 2,3-dimethyl glucose, 2,3,4-trimethyl glucose, and 2,3,4,6-tetramethyl glucose were required in studies on the structures of Dextrans I (17) and II (1), and it was found that, although many of these substances had been prepared previously, either the details of the procedures had been reported incompletely in the literature or the yields were low. These methylated glucose derivatives have now been synthesized by methods capable of giving higher reproducible yields and applicable not only to glucose but also to rarer carbohydrates.

Throughout these preparations, hydrolyses of the various intermediates were carried out using dilute sulphuric acid rather than dilute hydrochloric acid, the conventional hydrolytic agent, since sulphuric acid is easily removed as barium sulphate. Also Haworth methylation (in an atmosphere of nitrogen) was substituted for the laborious Purdie technique.

---

[1] *Manuscript received May 29, 1942.*

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada and the Canadian Pulp and Paper Association. Abstracted from theses presented by T. H. Evans and I. Levi in partial fulfilment of the requirements for the degrees of Doctor of Philosophy, 1941 and 1942, respectively.

[2] *Sessional Lecturer. Holder of Bursary under the National Research Council of Canada, 1938–1939, and a Studentship, 1939–1940.*

[3] *Postgraduate student and holder of Studentships, 1939–1940, 1941–1942, under the National Research Council of Canada.*

[4] *Formerly Sessional Lecturer, Department of Chemistry, McGill University. Present address: Department of Chemistry, Columbia University, New York.*

[5] *Professor of Industrial and Cellulose Chemistry, McGill University.*

2,3-Dimethyl-α-methyl glucoside (*14*) was prepared by the following series of reactions:

$$\text{Glucose} \xrightarrow[\text{HCl}]{CH_3OH} \alpha\text{-methyl glucoside} \xrightarrow[ZnCl_2\ \text{(anhyd.)}]{\text{benzaldehyde}} \text{4,6-benzylidene-}\alpha\text{-methyl glucoside} \xrightarrow[\text{NaOH}]{(CH_3)_2SO_4} \text{2,3-dimethyl-4,6-benzylidene-}\alpha\text{-methyl glucoside} \xrightarrow[H_2SO_4]{\text{dilute}} \text{2,3-dimethyl-}\alpha\text{-methyl glucoside.}$$

This procedure gives almost quantitative yields for amounts of material varying from 5 to 50 gm.

The benzylidene group is stable under the conditions of the Haworth methylation used, as shown by the high yield of product isolated.

2,3-Dimethyl-β-methyl glucoside was prepared by two different methods. The first may be summarized as follows:

$$\text{Glucose} \xrightarrow[CH_3\,CO\,ONa]{(CH_3CO)_2O} \text{penta-acetyl glucose} \xrightarrow[CH_3COOH]{\text{HBr}} \text{acetobromoglucose} \xrightarrow[Ag_2O]{CH_3OH} \text{tetra-acetyl-}\beta\text{-methyl glucoside} \xrightarrow{Ba(OH)_2} \beta\text{-methyl glucoside} \xrightarrow[ZnCl_2\text{(anhyd.)}]{\text{benzaldehyde}} \text{4,6-benzylidene-}\beta\text{-methyl glucoside} \xrightarrow[\text{NaOH}]{(CH_3)_2SO_4} \text{2,3-dimethyl-4,6-benzylidene-}\beta\text{-methyl glucoside} \xrightarrow[H_2SO_4]{\text{dilute}} \text{2,3-dimethyl-}\beta\text{-methyl glucoside.}$$

The final product in this case was crystalline, in contrast with the liquid product obtained by Oldham's method (20) using dilute hydrochloric acid as the hydrolytic agent.

Improved yields of tetra-acetyl-β-methyl glucoside were obtained by a modification of the Königs–Knorr reaction introduced by Reynolds and Evans (22). This included the addition of activated Drierite (16) as desiccant, and of iodine to catalyze the elimination of water.

The second method of preparation of 2,3-dimethyl-β-methyl glucoside was adapted from Oldham's (19) procedure and may be summarized as follows:

$$\text{2,3-Dimethyl-}\alpha\text{-methyl glucoside} \xrightarrow[H_2SO_4]{\text{dilute}} \text{2,3-dimethyl glucose} \xrightarrow[\text{pyridine}]{\text{benzoyl chloride}} \text{tribenzoyl-2,3-dimethyl glucose} \xrightarrow[CH_3COOH]{\text{HBr}} \text{dibenzoyl-bromo-2,3-dimethyl glucose} \xrightarrow[Ag_2O]{CH_3OH} \text{dibenzoyl-2,3-dimethyl-}\beta\text{-methyl glucoside} \xrightarrow[CH_3OH]{\text{K}} \text{2,3-dimethyl-}\beta\text{-methyl glucoside.}$$

Drierite and iodine (16, 22) were also added to the Königs-Knorr reaction mixture in this synthesis.

A new crystalline derivative of 2,3-dimethyl glucose, viz., 2,3-dimethyl gluconophenylhydrazide was prepared. 2,3-Dimethyl glucose was oxidized to the corresponding dimethyl gluconic acid by the method of Hudson and Isbell (12); the product was isolated by a slightly different procedure as a syrup (84% yield) and was converted to the crystalline phenylhydrazide in 80% yield.

There are two principal methods described in the literature for the preparation of *2,3,4-trimethyl methyl glucosides.*

Method I (23)

$$\alpha\text{-Methyl glucoside} \xrightarrow[\text{pyridine}]{\text{trityl chloride}} \text{6-trityl-}\alpha\text{-methyl glucoside} \xrightarrow[CH_3I]{Ag_2O} \text{2,3,4-trimethyl-}$$

$$\text{6-trityl-}\alpha\text{-methyl glucoside} \xrightarrow[HCl]{CH_3OH} \text{2,3,4-trimethyl-}\alpha\text{-methyl glucoside.}$$

The yields obtained by this procedure are generally low, particularly in the first step.

Method II (13)

$$\text{Levoglucosan} \xrightarrow[Ag_2O]{CH_3I} \text{2,3,4-trimethyl levoglucosan} \xrightarrow[HCl]{\text{dilute}} \text{2,3,4-trimethyl glucose}$$

$$\xrightarrow[HCl]{CH_3OH} \text{2,3,4-trimethyl-}\alpha\text{- and }\beta\text{-methyl glucosides.}$$

A modification of the latter procedure was used to synthesize 2,3,4-trimethyl-α- and β-methyl glucosides. In preliminary experiments, lower temperatures and shorter reaction periods were employed (cf. (26)) in the Haworth methylation of levoglucosan, but these led to low yields of incompletely methylated products. The normal procedure for Haworth methylation was therefore used and the 1,6-oxygen bridge in levoglucosan was found to be quite stable under these conditions. Trimethyl levoglucosan was hydrolysed to trimethyl glucose by means of dilute sulphuric acid.

The preparation of 2,3,4,6-tetramethyl glucose as described in the literature (6, 7, 8) is neither a quantitative nor a one-step procedure. The methylation of glucose as given by Haworth (6, 7, 8) results in low yields of partially methylated glucose. One methylation of glucose or α-methyl glucoside using the authors' modified procedure yielded a mixture of tetra-, tri-, and dimethyl methyl glucosides, separable by fractional distillation. Two such successive methylations of α-methyl glucoside gave a 91% yield of relatively pure 2,3,4,6-tetramethyl-α-methyl glucoside. This yield is considerably higher than those obtained previously (10, 25), indicating no appreciable degradation of the partially methylated glucoses during the Haworth methylation in a nitrogen atmosphere. Of the other reported methods, one (25) involves a Haworth methylation at the boiling point of carbon tetrachloride, used as solvent, while in another (10) a modified Haworth methylation is followed by Muskat methylation. The necessity for long reaction periods is evident.

It was found that the simplest method of extracting the methylated carbohydrates of relatively high methoxyl content (e.g., tetra- or trimethyl) present in the Haworth methylation reaction mixture was to reflux the latter with chloroform, and separate the chloroform layer. An additional advantage of this method was the fact that higher methylated products were found preferentially soluble in chloroform (cf. (18)), while those of lower methoxyl content remained in the water layer, which could be concentrated and remethylated.

Hydrolysis of 2,3,4,6-tetramethyl-α-methyl glucoside was carried out, with sulphuric rather than dilute hydrochloric acid, or steam and hydrochloric acid (25).

Experimental

*Synthesis of 2,3-Dimethyl-α-methyl Glucoside**

(a) α-Methyl glucoside. Previous preparations of this compound have been carried out by refluxing a glucose solution in anhydrous methanol containing 3% hydrogen chloride for only 4½ hr. (21) or by refluxing with 0.25% hydrogen chloride in methanol for 144 hr.(9). These procedures were modified, and refluxing for a total of 40 hr. with a hydrogen chloride concentration of 3% resulted in improved yields, about 75% of the theoretical. The hydrogen chloride was renewed at intervals, and the product was retreated in a manner similar to that previously described (9). The total yield of crude α-methyl glucoside from 200 gm. of glucose was 150 to 160 gm. (approximately 70% yield). After two recrystallizations from methanol, this product melted at 165 to 165.5° C.† (165 to 166° C. (21)); yield, 100 to 110 gm.

(b) 4,6-Benzylidene-α-methyl glucoside (5, 14). Merck benzaldehyde was redistilled in an atmosphere of nitrogen. B.p. 179.5° C. Dry finely ground α-methyl glucoside (25 gm., m.p. 165 to 166° C.), freshly distilled benzaldehyde (70 gm.), and finely ground fused zinc chloride (20 gm.) were shaken for six hours at room temperature. After standing 12 hr. at 0° C., the solution was poured in a fine stream into ice–water (400 cc.). The benzylidene compound separated as a fine white powder, which was filtered and washed with ice–water. The precipitate was then shaken with 10% sodium bisulphite solution (five 100 cc. portions) to free it from excess benzaldehyde, the wash liquors being decanted through the Büchner funnel. The benzylidene compound in the funnel was washed with a cold saturated solution of sodium bicarbonate (300 cc.), and ice–water (400 cc.), and finally with petroleum ether (b.p. 30 to 50° C.) to remove last traces of benzaldehyde. The yield of crude product was 28.5 gm. (78%). The 4,6-benzylidene-α-methyl glucoside (after one recrystallization from water) melted at 163 to 164° C. (161 to 162° C. (5)).

(c) 2,3-Dimethyl-4,6-benzylidene-α-methyl glucoside (5, 14). Crude 4,6-benzylidene-α-methyl glucoside, as obtained above, can be methylated in good

---

* *The procedures described for the synthesis of this compound are slight modifications of unpublished methods developed by previous workers in these laboratories, notably Dr. E. C. Fairhead and Dr. H. P. Godard.*

† *Melting points are uncorrected.*

yield without a preliminary recrystallization. 4,6-Benzylidene-α-methyl glucoside (12.5 gm.) was dissolved in acetone (75 cc.) at 40° C. and placed in a 500 cc. three-necked flask equipped with a stirrer and two burettes. Dimethyl sulphate (25 cc.) and 30% aqueous sodium hydroxide (75 cc.) were added in tenth portions at 10-min. intervals with stirring. After an additional hour's stirring, hot water (100 cc.) was added, and the solution was heated to 100° C. to destroy sodium methyl sulphate. The reaction mixture was cooled, and the methylated product filtered off. The yield of crude material was 12.4 gm. (90%). After one crystallization (88% yield, neglecting possible recovery from mother liquor) from petroleum ether (b.p. 100 to 110° C., 8 cc. per gm.), this product melted at 122 to 122.5° C. (122 to 123° C. (5)).

(d) 2,3-Dimethyl-α-methyl glucoside (14). 2,3-Dimethyl-4,6-benzylidene-α-methyl glucoside (10 gm.) was heated, with mechanical stirring, at 85 to 90° C. for one hour with 0.275 *N* sulphuric acid (100 cc.) under an atmosphere of nitrogen. The cooled reaction mixture was extracted five times with ether, using 20 cc. each time. The combined ether solutions were back-extracted with water (20 cc.). The aqueous solution was neutralized to Congo red with barium carbonate ground to a paste in water, and the barium sulphate centrifuged. The precipitate was washed with water (25 cc.) and recentrifuged. The combined aqueous solutions were filtered, and evaporated to dryness at 40° C. (15 mm.). The residue was extracted four times with hot benzene (using 40, 30, 20, and 10 cc. respectively). 2,3-Dimethyl-α-methyl glucoside crystallized out when the benzene solution was cooled. After one recrystallization from the same solvent, the product melted at 81.5 to 83° C.; yield, 6.5 gm. (90%).

2,3-Dimethyl-6-trityl-α-methyl glucoside was prepared according to a previously reported method (4).

2,3-Dimethyl Gluconophenylhydrazide

(a) 2,3-Dimethyl gluconic acid. 2,3-Dimethyl glucose was oxidized with aqueous bromine in the presence of barium benzoate (12). The aqueous solution was evaporated to dryness at 70° C. (20 mm.) after removal of inorganic salts and benzoic acid, and the pale yellow residual syrup extracted with hot anhydrous dioxane. A pale yellow syrup (OCH_3, 27.4%; theoretical for $C_6H_{10}O_5(OCH_3)_2$, 27.7%), non-reducing to Fehling's solution, was obtained after evaporation of the dioxane. Yield, 84%.

(b) 2,3-Dimethyl gluconophenylhydrazide. 2,3-Dimethyl gluconic acid (0.80 gm.) was dissolved in anhydrous ether (50 cc.) by refluxing for three hours. A fine white precipitate formed at once on the addition of freshly distilled phenylhydrazine (2.0 gm.), and after seven hours' refluxing it was removed by filtration. Additional material was recovered from the filtrate by further treatment with phenylhydrazine and concentration of the reaction mixture. The total yield of crude material was 1.08 gm. (96% of theoretical), which, after two recrystallizations from ethanol, separated as fine, short, white needles, m.p. 166.5 to 167° C. Yield, 0.9 gm. Found: C, 53.3; H, 7.1;

N, 9.3; OCH_3, 19.6%. Calc. for $C_{14}H_{22}O_6N_2$: C, 53.5; H, 7.0; N, 8.9; OCH_3, 19.7%.

Synthesis of 2,3-Dimethyl-β-methyl Glucoside

Method No. 1

β-Methyl glucoside was first prepared by a four-step procedure.

(a) Penta-acetyl glucose was prepared as previously described (2). The crude product was recrystallized from five parts of ethanol; yield, 67%. After two further recrystallizations, the pure product melted at 130 to 131° C. Various melting points have been reported (24) in the literature by different investigators, e.g., 132° C., 134 to 135° C.

(b) Acetobromoglucose was prepared as described previously (2). Recrystallization was effected by use of an ether–petroleum-ether mixture and a purer product was obtained in higher yield (73%) than by use of amyl alcohol (2). M.p. 87.5 to 88.5° C. (88° C. (15)).

In this preparation, the time required to isolate the product after dilution of the reaction mixture with water must be minimized as much as possible in order to obtain satisfactory yields. The pure product decomposes readily unless stored over phosphorus pentoxide in a desiccator.

(c) Tetra-acetyl-β-methyl glucoside was prepared by a Königs-Knorr reaction of methanol and acetobromoglucose in the presence of silver oxide following the method of Reynolds and Evans (22) for the preparation of α- and β-gentiobiose octa-acetates. The product was recrystallized from methanol; m.p. 101 to 102.5° C. (uncorrected); yield, 76%. Hudson and Dale (11) report a corrected m.p. of 104 to 105° C. after several recrystallizations.

(d) β-Methyl glucoside was obtained from tetra-acetyl-β-methyl glucoside in 93% yield by the method used for the preparation of α-methyl glucoside (3). The product was recrystallized from methanol by the addition of ether; m.p. 107.5 to 109° C. (110° C. (21)).

The preparation of 2,3-dimethyl-β-methyl glucoside from β-methyl glucoside followed, in general, the procedure outlined above for that of 2,3-dimethyl-α-methyl glucoside from α-methyl glucoside.

(e) Crude *4,6-benzylidene-β-methyl glucoside (5)* was obtained as a gummy product. After trituration in a mortar with sodium bisulphite solution, the yield of crude material was 67%. Recrystallized from water, the product melted at 199 to 201° C. (194° C. and 205° C. (5)).

(f) 2,3-Dimethyl-4,6-benzylidene-β-methyl glucoside. 4,6-Benzylidene-β-methyl glucoside was not sufficiently soluble in acetone at 40° C. to allow of methylation with dimethyl sulphate and sodium hydroxide; dioxane was therefore used as a solvent for the Haworth methylation. The yield of crude material (one experiment only) was about 50%. Considerable losses resulted on recrystallization from petroleum ether (b.p. 100 to 110° C.) and from ethanol; m.p. 132 to 133° C. (132 to 135° C. (20)).

(g) 2,3-Dimethyl-β-methyl glucoside (19, 20). 2,3-Dimethyl-4,6-benzylidene-β-methyl glucoside (0.9 gm., m.p. 132 to 133° C.), ethanol (50 cc.) and 0.27 *N* sulphuric acid (20 cc.) were heated at 60 to 65° C. for one and one-half hours in an atmosphere of nitrogen. The product was isolated by the method used for the α-isomer. It could not be crystallized from petroleum ether (b.p. 60 to 70° C.) nor from chloroform on the addition of petroleum ether (b.p. 30 to 50° C.). Yield, 0.5 gm. (78%); OCH_3, 38.9%. Distillation of the oil in a Späth bulb (bath temperature 125° C./0.003 mm.) yielded a colourless oil; OCH_3, 41.0% (theoretical, 41.9%). This material crystallized on standing; m.p. 60 to 61° C. (62 to 64° C. (19)).

Method No. 2

This was a modification of that of Oldham (19) discussed above.

(a) 2,3-Dimethyl glucose (14). 2,3-Dimethyl-α-methyl glucoside (10 gm., m.p. 82 to 83° C.) was heated with normal sulphuric acid (400 cc.) in an atmosphere of nitrogen for 16 hr. in a water-bath at 100° C. The rotation was constant during the last two hours, and the reaction was adjudged complete. The product was isolated according to the procedure outlined for 2,3-dimethyl-α-methyl glucoside except that no preliminary ether extraction was necessary and methanol was substituted for benzene. Evaporation of the methanol yielded 9.2 gm. (quantitative); OCH_3, 29.7% (theoretical, 29.8%).

(b) Tribenzoyl-2,3-dimethyl glucose, dibenzoyl-2,3-dimethyl-β-methyl glucoside and *2,3-dimethyl-β-methyl glucoside* were prepared according to Oldham's procedure (19), except that the improved Königs-Knorr technique (22) mentioned above was again used. After one recrystallization from carbon tetrachloride the 2,3-dimethyl-β-methyl glucoside melted at 60 to 62° C.

Preparation of 2,3,4-Trimethyl Glucose

(a) 2,3,4-Trimethyl Levoglucosan (13)

Levoglucosan (10 gm., m.p. 177° C.) was dissolved in water, and the solution stirred in an atmosphere of nitrogen. Dimethyl sulphate (10 cc.) was added immediately, and sodium hydroxide (20 cc. of a solution of 100 gm. in 175 cc. water) added dropwise during two hours. Dimethyl sulphate and sodium hydroxide (20 cc. and 40 cc. respectively) were added dropwise and in approximately equivalent amounts during 1½ hr. The temperature was slowly raised to 60° C. during the next two hours, then dimethyl sulphate (10 cc.) added slowly. The temperature was kept at 60° C. for four hours, and the reaction mixture stirred at 50° C. for 12 hr. Following this it was about half neutralized with 50% sulphuric acid, heated at 100° C. for one-half hour, cooled below 20° C. and rendered slightly alkaline to phenolphthalein by the addition of 50% sulphuric acid. The reaction mixture was exhaustively extracted by refluxing with several successive portions of chloroform (e.g., 100, 75, 50, 50, and 50 cc.). The combined chloroform extracts were dried and evaporated under reduced pressure; yield, 10 gm. (*A*). The aqueous mother liquor was cooled at −15° C., sodium sulphate removed and the solution concentrated (*B*). The methylated levoglucosan (*A*) was not completely crystalline, since it was not fully methylated. After two recrystallizations from ether, the product melted at 59° C. Material recovered from the mother liquors was added to the concentrated aqueous methylation solution (*B*) and both were again methylated using dimethyl sulphate and sodium hydroxide as described above. The total yield of product from all these operations was 10 gm. approximately (80%). On recrystallization from ether, it melted at 59° C.; yield, 8 gm.

(b) 2,3,4-Trimethyl Glucose

Trimethyl levoglucosan (5 gm., m.p. 59° C.) in 3.6% sulphuric acid (100 cc.) was heated at 100° C. for 17 hr. (constant rotation). The product was isolated according to the procedure outlined for 2,3-dimethyl glucose, except that acetone replaced methanol as solvent. Yield (light-yellow oil), 5.1 gm. (96%): OCH_3, 41.6%; theoretical, 41.9%.

Extensive decomposition of 2,3,4-trimethyl glucose resulted when this compound was distilled (even in an atmosphere of nitrogen) at temperatures and pressures lower than those used by Irvine and Oldham (13). However, since the 2,3,4-trimethyl glucose prepared by the method outlined above is relatively pure it was employed without further purification.

(c) 2,3,4-Trimethyl-α- and β-Methyl Glucosides from 2,3,4-Trimethyl Glucose

2,3,4-Trimethyl glucose (5.0 gm.) dissolved in anhydrous methanol (140 gm.) containing anhydrous hydrogen chloride (4 gm.) was refluxed for 17 hr. at which time the solution was no longer reducing to Fehling's solution. Addition of silver carbonate (5 gm.) rendered the solution slightly alkaline to Congo red. The mixed glucosides were separated from silver salts and methanol in the usual manner; yield, 4.9 gm. (92%).

This product was fractionally distilled, in an atmosphere of nitrogen, through a Widmer column, bath temperature 125 to 185° C. (0.07 mm.); residue, less than 5%. The first portion of the distillate was predominantly crystalline 2,3,4-trimethyl-β-methyl glucoside. When crystallized from petroleum ether (b.p. 30 to 50° C.) containing about 5% ether, this melted at 93 to 94° C. (94° C. (4)). The remainder of the distillate was largely 2,3,4-trimethyl-α-methyl glucoside: OCH_3, 52.1%; theoretical, 52.6%.

Preparation of 2,3,4,6-Tetramethyl Glucose

(a) 2,3,4,6-Tetramethyl-α-methyl Glucoside

This was prepared by Haworth methylation of α-methyl glucoside following the procedure given above for the methylation of levoglucosan. The product was recovered by chloroform extraction (as described above) in such amount that remethylation of the mother liquor was not advantageous. Yield of crude product, 35.8 gm. from 30 gm. α-methyl glucoside; n_D^{22}, 1.4525 (tetramethyl α-methyl glucoside, n_D^{20}, 1.4460 (25); trimethyl methyl glucoside, 1.4578).

The crude product was remethylated; yield, 35.3 gm. (91%). n_D^{22}, 1.4458. This material was fractionally distilled through a Widmer column, and 32.1 gm. obtained; b.p. 91.5 to 93° C. (0.5 to 0.6 mm.) (bath temperature, 130 to 140° C.); OCH_3, 59.8%. Redistillation at 90.5 to 93° C. (0.5 to 0.6 mm.) (bath temperature, 120° C.) yielded 31.8 gm. n_D^{22}, 1.4453; OCH_3, 61.3%, theoretical 62.0%.

Two Haworth methylations of glucose following the same procedure gave high yields of tetramethyl methyl glucosides when the methylations were carried out in an atmosphere of nitrogen and at a lower preliminary temperature (20 to 30° C. for the first three hours during which time too great an excess of sodium hydroxide was avoided). Under these conditions, the glucosidic hydroxyl is methylated before extensive decomposition occurs (8).

(b) 2,3,4,6-Tetramethyl Glucose

2,3,4,6-Tetramethyl-α-methyl glucoside (10 gm.) was hydrolysed at 100° C. with 5% sulphuric acid (200 cc.) until constant rotation was reached (about 12 hr.). The product was isolated as described above for 2,3-dimethyl glucose, ether being used as the final solvent. The product, partially crystalline, was dissolved in petroleum ether (b.p. 30 to 50° C.) containing 5 to 10% ether, from which a portion of the product crystallized. The non-crystalline material in the mother liquor was rehydrolysed, and recrystallized from the petroleum ether and ether mixture. The total yield of crystalline material was approximately 8 gm. (76%); OCH_3, 52.4% (theoretical, 52.5%). After one additional recrystallization, the product melted at 90 to 91° C. (90 to 93° C. (25)).

References

1. Evans, T. H. Unpublished results.
2. Fischer, E. Ber. 49 : 584-585. 1916.
3. Fischer, E. and Armstrong, E. F. Ber. 34 : 2885-2900. 1901.
4. Fowler, F. L., Buckland, I. K., Brauns, F., and Hibbert, H. Can. J. Research, B, 15(11) : 486-497. 1937.
5. Freudenberg, K., Toepffer, H., and Andersen, C. C. Ber. 61 : 1750-1760. 1928.
6. Haworth, W. N. J. Chem. Soc. 107 : 8-16. 1915.
7. Haworth, W. N. and Leitch, G. C. J. Chem. Soc. 113 : 188-199. 1918.
8. Haworth, W. N. and Sedgwick, W. G. J. Chem. Soc. 2573-2580. 1926.
9. Helferich, B. and Schäfer, W. Org. Syntheses, 6 : 64-65. 1926.
10. Hendricks, B. C. and Rundle, R. E. J. Am. Chem. Soc. 60(10) : 2563-2564. 1938.
11. Hudson, C. S. and Dale, J. K. J. Am. Chem. Soc. 37(5) : 1264-1270. 1915.
12. Hudson, C. S. and Isbell, H. S. J. Am. Chem. Soc. 51(7) : 2225-2229. 1929.
13. Irvine, J. C. and Oldham, J. W. H. J. Chem. Soc. 119 : 1744-1759. 1921.
14. Irvine, J. C. and Scott, J. P. J. Chem. Soc. 103 : 575-586. 1913.
15. Karrer, P., Nägeli, C., and Smirnoff, A. P. Helv. Chim. Acta, 5 : 141-146. 1922.
16. Kreider, L. C. and Evans, W. L. J. Am. Chem. Soc. 58(5) : 797-800. 1936.

17. Levi, I., Hawkins, W. L., and Hibbert, H. J. Am. Chem. Soc. 64(8):1959-1962. 1942.
18. Macdonald, J. Y. J. Am. Chem. Soc. 57(4) : 771-772. 1935.
19. Oldham, J. W. H. J. Am. Chem. Soc. 56(6) : 1360-1362. 1934.
20. Oldham, J. W. H. and Rutherford, J. K. J. Am. Chem. Soc. 54(1) : 366-378. 1932.
21. Patterson, T. S. and Robertson, J. J. Chem. Soc. 300-302. 1929.
22. Reynolds, D. D. and Evans, W. L. J. Am. Chem. Soc. 60(10) : 2559-2561. 1938.
23. Robertson, A. and Waters, R. B. J. Chem. Soc. 1709-1714. 1931.
24. Vogel, H. and Georg, A. Tabellen der Zucker und ihrer Derivative. J. Springer, Berlin. 1931.
25. West, E. S. and Holden, R. F. Org. Syntheses, 20 : 97-100. 1940.
26. Zemplén, G. and Braun, G. Ber. 58 : 2566-2570. 1925.

KINETICS OF THE ALKALINE HYDROLYSIS OF PROPIONITRILE[1]

By B. S. RABINOVITCH[2] AND C. A. WINKLER[3]

Abstract

Some contradictory points recorded for the alkaline hydrolysis of nitriles have been clarified by a study of propionitrile hydrolysis in aqueous sodium hydroxide solutions of concentration 0.3 to 4 *N*. It has been shown that the rate of alkaline hydrolysis of propionitrile is given by the rate of formation of total ammonia and intermediate amide and not by that of ammonia alone. The relative rates of propionitrile and propionamide hydrolysis were found to be approximately 1 : 10 over the whole alkali concentration range. The bimolecular velocity constant is essentially independent of alkali concentration. An activation energy of 20,300 cal. was determined for the reaction in 0.65 *N* alkali.

Introduction

The hydrolysis of nitriles proceeds through the amide to yield the corresponding acid and ammonia:

$$\text{Nitrile} \xrightarrow{H_2O} \text{amide} \xrightarrow{H_2O} \text{acid} + \text{ammonia.}$$

The existing state of knowledge of the reaction in alkaline solutions is unsatisfactory. Both the relative rates of the consecutive reactions of simple aliphatic nitriles and amides (7, 10), and the occurrence of an induction period in the nitrile hydrolysis (10, 12), appear to be in doubt. With respect to the latter point, data on the alkaline hydrolysis of substituted acetonitriles (1, 2), of which those of the second paper only were accessible, have been stated to follow the bimolecular equation. However, since these velocity data refer usually to less than 5% reaction and display deviations in this range as high as 15% from the mean, this evidence appears unsatisfactory.

It has been found (8, 11) for the acid hydrolysis of nitriles, which has been studied in some detail, that the activation energy depends on acid concentration, and that the variation of rate with acid concentration could be related to the activation energy change. Existing studies of the effect of temperature on the rate of hydrolysis in alkaline solutions have been restricted to a range of only 7° C. for acetonitrile and propionitrile (10), and to a range of only 10° C. for certain substituted acetonitriles (1, 2), at one alkali concentration in each instance.

In view of the contradictory points mentioned above, it seemed of interest to investigate the alkaline hydrolysis of propionitrile, for which nitrile the acid studies were the most complete, and to examine the Arrhenius parameters over a range of alkali concentration. Owing to circumstances beyond control

---

[1] *Manuscript received in original form February 4, 1942, and as revised, May 11, 1942. Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.*

[2] *Postgraduate student, and holder of a Studentship and Fellowship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry.*

of the authors, the study had to be terminated before the Arrhenius parameters could be examined. It was uncertain when further work on the problem might be possible, and the results obtained to date are presented since they clarify to a large extent the controversial points.

Materials and Procedure

An aqueous, saturated solution of reagent grade sodium hydroxide was prepared, the carbonate precipitated, and the alkali standardized by means of constant boiling hydrochloric acid. Solutions of known strength were prepared by dilution. All solutions were protected from air.

Propionitrile was obtained commercially and fractionated to a constant boiling point. Aqueous solutions were prepared by direct weight, such that nitrile concentrations in the reaction mixtures were approximately 0.3 *N*.

Equal volumes of alkali and nitrile solutions were mixed at 0° C., and Pyrex tubes were filled, sealed, and immersed in thermostats regulated to 0.1° C. The volume change on mixing was determined with the aid of density–percentage data for sodium hydroxide in International Critical Tables, the nitrile solution being treated as water. All concentrations have been taken as at 25° C. Temperatures were measured with standard thermometers. An experimentally determined correction was made for the time required for solutions to warm to reaction temperature. From time to time, tubes were removed, quickly cooled, and analysed. It was found that the products of reaction exert a retarding effect, so that reaction was allowed to proceed to only about 60% completion.

In following the course of the reaction, analysis was made either for ammonia alone, or for total amide and ammonia by methods described earlier (11). No difficulty was experienced from loss of ammonia upon opening the tubes, at alkali concentrations below 2 *N*. At 4 *N*, the results tended to be erratic, although in the run at this concentration recorded below, which is a better one, the individual *k* values showed an average deviation from the mean of only 3%.

Results and Discussion

The results in Table I show that the rate of alkaline hydrolysis, as determined by formation of ammonia alone, is dependent on the hydrolysis of the intermediate amide. An induction period in the rate is observed, although the velocity constants approach the true values obtained by determination of total amide and ammonia. In the latter case, no induction period is evident and the reaction follows the bimolecular expression. The bimolecular constants recorded in Table II have been determined in this manner. The average deviation of the individual values from the recorded mean was about 1 to 2%.

Following the discussion outlined for the acid hydrolysis of propionitrile (11), the magnitude of the induction periods indicates that the relative rates of propionitrile and propionamide hydrolysis, over the concentration range,

TABLE I

DATA SHOWING NATURE OF THE INDUCTION PERIODS AND RELATIVE RATES OF PROPIONITRILE AND PROPIONAMIDE HYDROLYSIS

Concentration of alkali, normality	Temperature, °C.	Analytical procedure. A—ammonia only AA—amide and ammonia	$k \times 10^3$					
			NH$_3$* %					
			10 – 20	20 – 30	30 – 40	40 – 50	50 – 60	60 – 70
0.325	59.6	A	171	240	245		298	318
	59.6	AA	400	390	381	384	386	
0.650	39.5	A	27.3	36.2	44.2	47.2	48.0	
	39.5	AA	56.8	58.2	55.1	56.9	57.4	57.0
1.840	39.5	A	32.5 35.9	44.0	48.1	51.1		
	39.5	AA	59.6	58.7	59.4	60.0	59.1	

* *Refers to runs analysed for ammonia only.*

TABLE II

BIMOLECULAR VELOCITY CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE IN SODIUM HYDROXIDE SOLUTIONS

Concentration of alkali, normality	Concentration of nitrile, normality	Temperature, °C.	$k \times 10^2$ hr.$^{-1}$
0.325	0.2175	39.5	5.58
0.650	0.3020	39.5	5.69
0.650	0.2911	29.7	1.88
0.650	0.2716	49.6	15.1
0.650	0.3020	59.6	39.1
0.923	0.2721	39.5	5.66
1.840	0.3054	39.5	5.94
4.330	0.2963	39.5	5.96

are of the order of 1 : 10, within a factor of about two. This is confirmed by comparison of the present data with those of a number of investigators for the alkaline hydrolysis of amides (3, 6, 10). It is permissible to use data for acetamide hydrolysis, which are more numerous, for this purpose, since its velocity is within 10 to 20% of that for propionamide. Since the velocity of alkaline hydrolysis of both nitriles (Table II) and amides (4, 5) are independent of, or vary but slowly with, alkali concentration, the above approximate rate ratio should also apply over a wider concentration range than that considered here.

The induction period found in the present study, by determination of ammonia alone, agrees with the results of Reitz (12), but not with those of

Peskoff and Meyer (10) who did not observe it, although in both instances the reaction was followed by ammonia production. The reason for this discrepancy in the work of Peskoff and Meyer is not apparent. Furthermore, although their data indicate that the amide is hydrolysed faster than the nitrile (e.g., $k_{propionamide} : k_{propionitrile} : : 0.1353 : 0.00888$ (1 *N* potassium hydroxide, 25° C.)), for some reason these authors conclude that only the velocity of amide hydrolysis can be determined by their measurements. Kilpi (7) has noted this discrepancy, and has pointed out that on the basis of their data the velocity of the slower nitrile reaction has been measured. The present work shows that at all alkali concentrations considered, analysis must be made for total amide and ammonia to determine the velocity of nitrile hydrolysis.

The reaction velocity is essentially independent of alkali concentration (Table II) within the range considered and does not decrease at concentrations above 0.8 *N*, as has been reported by Reitz. The rate behaviour of the alkaline hydrolysis differs markedly from that in acid solution, where a very rapid increase in rate with acid concentration was found (11).

The data at 0.65 *N* alkali give an activation energy of 20,300 cal., obtained from the Arrhenius line. Calculation of the results of Peskoff and Meyer, for a range of 7° C. in 1 *N* potassium hydroxide, yields the approximate value 18,500 cal. for propionitrile and 19,100 for acetonitrile. Had circumstances permitted, it would have been desirable to find the activation energy at higher alkali concentrations, to determine whether it is dependent on concentration.

The activation energy for the alkaline hydrolysis of propionitrile is approximately 5000 cal. less than that for the acid hydrolysis, at the same catalyst concentration (8). This difference is in accord with the generally observed lowering of the activation energy for alkaline hydrolysis reactions as compared with acid hydrolysis (9, p. 253).

References

1. ANGELESCU, E., VASILIU, G., and RADVAN, S. Bull. sect. sci. acad. roumaine, 22 : 220. 1939.
2. ANGELESCU, E., VASILIU, G., and RADVAN, S. Bull. sect. sci. acad. roumaine, 22 : 411. 1940.
3. CALVET, E. J. chim. phys. 30 : 198-212. 1933.
4. CALVET, E. and CALVET, E. Compt. rend. 199 : 1313-1315. 1934.
5. CROCKER, J. C. and LOWE, F. H. J. Chem. Soc. 91 : 952-962. 1907.
6. HOEFLAKE, J. M. A., SCHEFFER, F. E. C., VAN NOUHUYS, M. J. R. H., and POSTHUMUS-BRUYN, J. C. Rec. trav. chim. 51 : 673-691. 1932.
7. KILPI, S. Z. physik. Chem. 86 : 740-743. 1914.
8. MCLEAN, J. D., RABINOVITCH, B. S., and WINKLER, C. A. Can. J. Research, B, 20(8): 168-173. 1942.
9. MOELWYN-HUGHES, E. A. Kinetics of reactions in solution. Oxford University Press, London. 1933.
10. PESKOFF, N. and MEYER, J. Z. physik. Chem. 82 : 129-171. 1913.
11. RABINOVITCH, B. S., WINKLER, C. A., and STEWART, A. R. P. Can. J. Research, B, 20(7) : 121-132. 1942.
12. REITZ, O. Z. physik. Chem. A, 183 : 371-391. 1939.

ENZYME INHIBITION BY DERIVATIVES OF PHENOTHIAZINE

II. INHIBITION OF CHOLINESTERASE[1]

By H. BRUCE COLLIER[2] AND DELLA E. ALLEN[3]

Abstract

The cholinesterase activity of horse serum is strongly inhibited by phenothiazone and by some phenothiazine alkyl-sulphonium salts. The magnitude of this inhibition is about equal to that produced by methylene blue and by acriflavine. Alkaline phosphatase and serum lipase are not affected.

The possible relation of this property of phenothiazine derivatives to certain nervous symptoms observed in treated pigs, and to insecticidal and anthelmintic action, is discussed.

The first paper in this series described the inhibition of catalase and of cytochrome oxidase by leuco-phenothiazone (3-hydroxy thiazine) (3), and a preliminary note has been published on the inhibition of succinic dehydrogenase by phenothiazone (3-oxythiazine) (4).

The well known effect of quaternary ammonium compounds on cholinesterase suggested that the phenothiazine oxidation products might exert a similar action, even though the N atom in these derivatives is not basic. Raventós (15) and Rentz (16) have reported an inhibition of the enzyme by methylene blue, and Massart and Dufait (12) have recently described inhibitions by this and other basic dyes. (Only an abstract of the last mentioned paper has been seen.)

The present paper describes a strong inhibition of horse-serum cholinesterase by phenothiazone and by sulphonium derivatives of phenothiazine. These compounds had no effect upon kidney phosphatase (at pH 9), or upon horse-serum lipase (acting upon tributyrin); therefore the inhibition does not apply to esterases in general.

Cholinesterase is the only *hydrolytic* enzyme thus far found susceptible to the action of phenothiazine derivatives.

Experimental

Method

The source of enzyme was fresh horse serum and the activity was measured manometrically in a Summerson differential manometer by a modification of the method of Stedman and Stedman (18).

A measured portion of the serum, usually 0.1 ml., was diluted to 2.0 ml. with a saline solution of the following composition: 0.85% sodium chloride, 0.025 *M* sodium bicarbonate, 0.001 *M* calcium chloride, 0.001 *M* manganese

---

[1] *Manuscript received in original form June 17, 1942, and as revised, August 1, 1942.*
Contribution from the Institute of Parasitology, McGill University, Macdonald College, Que., with financial assistance from the National Research Council of Canada.

[2] *Lecturer.*

[3] *Research Assistant.*

chloride. (This concentration of divalent ions was found to give maximum activity; potassium chloride up to 0.01 *M* had no effect.) The diluted serum was equilibrated for 30 min. at 37° C. with a 95%-nitrogen–5%-carbon-dioxide mixture, and was then mixed with 0.2 ml. of 2.5% acetylcholine bromide from the side arm of the reaction vessel. The final pH was 7.3, and the final substrate concentration was 0.01 *M*, which was found to give virtually as rapid hydrolysis as 0.05 *M* concentration.

The rate of carbon dioxide production was read differentially against a blank, identical with the above except for the addition of 10^{-6} *M* eserine* to inhibit the enzyme. Readings were taken every five minutes for 15 min. The rate of hydrolysis was found to be linear, and proportional to enzyme concentration, under these conditions; therefore the enzyme activity was expressed as μl. of carbon dioxide in 15 min. at 37° C.

The inhibitors to be tested were dissolved in the saline in both vessels (having been first neutralized, if necessary), and were therefore in contact with the enzyme for 30 min. before the beginning of hydrolysis.

Preparations

Phenothiazone was prepared by oxidation of phenothiazine with ferric chloride (14). It was recrystallized from hot water and gave a melting point (corr.) of 165° C. Thionol (3-oxy-9-hydroxy thiazine) was prepared by the method of Bernthsen (2); it was partially purified by precipitation from alkaline solution with acid.

The S-methyl and S-ethyl sulphonium derivatives of phenothiazine were prepared by Kehrmann and Dardel's method (9), being isolated as the perchlorates. N-methyl phenothiazine was prepared by the method of Bernthsen (2).

Inhibition by Eserine

The inhibitory power of eserine (physostigmine), one of the most powerful inhibitors known, was determined under the conditions of these experiments, in order to make accurate comparison with the other inhibitors. The results may be summarized briefly as follows:

5×10^{-9} *M* eserine 20% inhibition
5×10^{-8} *M* eserine 66% inhibition
5×10^{-7} *M* eserine 91% inhibition

By interpolation it is found that 50% inhibition is produced by approximately 2.5×10^{-8} *M* concentration of eserine.

Effect of Phenothiazine Derivatives

The effect of methylene blue, phenothiazone, and thiazine methyl-sulphonium perchlorate on the enzyme is indicated in Tables I, II, and III. From these figures the concentrations necessary to produce 50% inhibition are found to be 1.2×10^{-6} *M*, 6.7×10^{-5} *M*, and 1.6×10^{-6} *M*, respectively.

---

* *Physostigmine sulphate, kindly supplied by Merck & Co. Ltd., Montreal.*

TABLE I

EFFECT OF METHYLENE BLUE ON CHOLINESTERASE

Concentration of dye, $M \times 10^7$	Enzyme activity, $\mu l.\ CO_2$	Inhibition, percentage
0	100	0
6	94	6
9	80	20
12	49	51
17	28	72
24	21	79
60	16	84
120	0	100

TABLE II

INHIBITION BY PHENOTHIAZONE

Concentration, $M \times 10^5$	Enzyme activity, $\mu l.\ CO_2$	Inhibition, percentage
0	158	0
1.7	129	18
3.3	121	23
6.7	79	50
16.7	31	80
48.0	0	100

TABLE III

INHIBITION BY PHENOTHIAZINE METHYL-SULPHONIUM PERCHLORATE

Concentration, $M \times 10^8$	Enzyme activity, $\mu l.\ CO_2$	Inhibition, percentage
0	110	0
1.2	109	1
12.0	83	25
120.0	62	44
1200.0	17	85
12000.0	7	94
24000.0	0	100

Ethyl-sulphonium perchlorate gave an inhibition similar to that with the methyl derivative. Thionol and N-methyl phenothiazine were without effect.

Other Compounds

Indole, sulphanilamide, and *p*-hydroxylamino benzenesulphonamide were without effect upon the enzyme. Acriflavine (National Aniline and Chemical Co., New York), was found to be a powerful inhibitor, as indicated in Table IV.

TABLE IV

EFFECT OF ACRIFLAVINE ON CHOLINESTERASE

Concentration, $M \times 10^7$	Enzyme activity, μl. CO_2	Inhibition, percentage
0	109	0
5	99	9
50	65	40
100	39	64
500	4	96
1000	0	100

Discussion

The results of these experiments have been summarized in Table V, where the molar concentrations necessary to produce 50% inhibition of the activity of the serum cholinesterase are recorded. It may be concluded that the phenothiazine derivatives described are powerful inhibitors of cholinesterase, similar to strychnine (8) and morphine (1). Phenothiazone, which is not basic, is a somewhat weaker inhibitor than methylene blue, which contains a quaternary N atom, or the alkyl-sulphonium derivatives, which have a ternary S atom. In the case of the methyl-sulphonium salt, the great range of concentration observed, approximately 10^{-8} to 10^{-4} M, is worthy of note.

TABLE V

CONCENTRATIONS OF COMPOUNDS GIVING 50% INHIBITION OF CHOLINESTERASE

Compound	Concentration	
	Molar	Mg. per litre
Eserine*	2.5×10^{-8}	0.007
Methylene blue	1.2×10^{-6}	0.45
Thiazine methyl-sulphonium ion*	1.6×10^{-6}	0.37
Acriflavine	6.6×10^{-6}	1.7
Phenothiazone	6.7×10^{-5}	14.0

* *Calculated as the free base.*

The physiological significance of these findings cannot be adequately assessed without further investigation. The recent reviews of Nachmansohn (13) and of Glick (6) discuss the role of cholinesterase in the mediation of nerve impulses at synapses and neuromuscular junctions. It is therefore a possibility that phenothiazine derivatives may act upon the nervous system through inhibition of the cholinesterase. Or the compounds may be antagonistic to the action of acetylcholine, through a similarity of chemical structure (which would also explain the enzyme inhibition). These substances presumably have a pharmacological action similar to that of the "onium" salts, as described by Raventós (15) and by Ing (7).

Evidence for an apparent curariform action of phenothiazine may be found in the observation of H. O. J. Collier (5), that a one in ten million solution (probably oxidized to phenothiazone) increases the "block" in a neuromuscular preparation of the crab, *Carcinus moenas.* In addition, several groups of workers (10, 19) have reported nervous symptoms in pigs after phenothiazine treatment—partial posterior paralysis and inco-ordination.

Whether this effect of phenothiazine derivatives on cholinesterase is related to their insecticidal (17) or anthelmintic action is also a matter for speculation at the present time. McIlwain (11) has suggested that parasitic worms are narcotized by anthelmintic drugs, but the mechanism of this action has not yet been elucidated.

References

1. Bernheim, F. and Bernheim, M. L. C. J. Pharmacol. 57 : 427-436. 1936.
2. Bernthsen, A. Ann. 230 : 73-211. 1885.
3. Collier, H. B. Can. J. Research, B, 18 : 345-350. 1940.
4. Collier, H. B. and Allen, D. J. Biol. Chem. 140 : 675-676. 1941.
5. Collier, H. O. J. Nature, 146 : 232-233. 1940.
6. Glick, D. Biol. Symposia, V : 213-233. 1940.
7. Ing, H. R. Physiol. Rev. 16 : 527-544. 1936.
8. Kaswin, A. Compt. rend. soc. biol. 130 : 859-862. 1939.
9. Kehrmann, F. and Dardel, J. H. Ber. 55 : 2346-2356. 1922.
10. McCulloch, E. C. and Seghetti, L. Vet. Med. 37 : 80-84. 1942.
11. McIlwain, H. Lancet, 242 : 412-415. 1942.
12. Massart, L. and Dufait, R. Enzymologia, 9 : 364-368. 1941. Chem. Abstracts, 36 : 792. 1942.
13. Nachmansohn, D. Yale J. Biol. Med. 12 : 565-589. 1940.
14. Pummerer, R. and Gassner, S. Ber. 46 : 2310-2327. 1913.
15. Raventós, J. Quart. J. Exptl. Physiol. 27 : 99-111. 1937.
16. Rentz, E. Arch. exptl. Path. Pharmakol. 196 : 148-160. 1940. Chem. Abstracts, 35 : 2607. 1941.
17. Smith, L. E., Munger, F., and Siegler, E. H. J. Econ. Entomol. 28 : 727-728. 1935.
18. Stedman, E. and Stedman, E. Biochem. J. 29 : 2107-2111. 1935.
19. Thorning, W. M., Morrill, C. C., and Boley, L. E. Vet. Med. 37 : 120-122. 1942.

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 20, SEC. B. OCTOBER, 1942 NUMBER 10

LES GLUCIDASES ET LES GLUCIDES D'*IPOMOEA BATATAS* ET DE *SOLANUM TUBEROSUM*[1]

Par Elphège Bois[2] et Jean Savary[3]

Résumé

L'action des jus dialysés d'*Ipomoea Batatas* et de *Solanum tuberosum* sur l'amidon produit du maltose, du sucrose, et du sucre interverti. Ces jus contiennent une maltogène-amylase, une sucrogène amylase, et l'invertase. La maltase est absente. Dans ces patates cependant on ne trouve pas de maltose mais du sucrose et du sucre interverti. L'hydrolyse enzymatique conduira à une nouvelle hypothèse de la constitution de l'amidon.

Introduction

La présence d'une amylase dans *Solanum tuberosum* est reconnue depuis les travaux de Windish et Jetter (12, 13). Gore a démontré que l'*Ipomoea Batatas* contient aussi une amylase (6).

Mais la reconnaissance d'autres glucidases et des produits formés par le travail de ces amylases n'amène pas toujours l'accord entre les chercheurs. Il suffit de rappeler les publications de Doby et Bodnar (4), Gore (7), Miyake (9) et Nelson et Auchincloss (10).

Comme l'activité de ces amylases est tantôt appréciée par la coloration avec l'iode, tantôt par la mesure du pouvoir réducteur, le plus souvent exprimé en maltose (5); cela explique déjà les résultats variés obtenus. Nous verrons qu'en plus des conditions variables, des facteurs nouveaux peuvent influencer ces résultats.

Hanes (8) montre aussi que l'amylase de la patate ordinaire est accompagnéè d'une phosphorylase qui transforme l'amidon en glucose-1-phosphate lequel peut ensuite passer jusqu'aux hexose-6-phosphates réducteurs et fructose diphosphate (11). Nous avons été conduits à l'étude des glucidases et des glucides de la patate douce et de la patate ordinaire à la suite de la reconnaissance dans la sève d'érable, d'une amylase qui hydrolyse l'amidon en sucrose (2).

Partie expérimentale

Les solutions d'amidon sont préparées à partir d'amidon soluble; sa suspension dans l'eau froide est jetée dans un grand volume d'eau bouillante; après refroidissement, du toluène est additionné en excès.

---

[1] *Manuscrit original reçu le 2 mars 1942, et sous forme revisée le 22 juin 1942.*
Contribution du Laboratoire de Biochimie, Faculté des Sciences, Université Laval, Québec, Qué.

[2] *Professeur de biochimie.*

[3] *Etudiant gradué (bourse Price).*

Les tampons sont constitués de solutions $M/15$ de phosphate de sodium, de potassium, et d'acide phosphorique.

Le pouvoir réducteur des essais est déterminé par la méthode de Luff et Scholl (3, p. 830) et exprimé en milligrammes de glucose ou en millilitres de thiosulfate de sodium $N/20$.

La préparation des extraits

Des patates sucrées (*Ipomoea Batatas*) et des patates ordinaires (*Solanum tuberosum*) sont rapées, séchées à la température de la chambre, réduites en poudre suffisamment fine pour être tamisée à 40 mailles. Cent grammes de la poudre sont agités avec 500 ml. d'eau additionnée de toluène, puis macérés à la glacière pendant 24 hr. Après filtration sur toile, les jus (400 ml. de chacun) sont mis à dialyser dans des tubes de cellophane contre l'eau du robinet.

Signalons que le jus obtenu par pression des patates a un pH d'environ 5.0, tandis que celui que nous obtenons par macération de la poudre est de 6.5 environ.

Après une dialyse de deux jours, les jus sont concentrés à 400 ml. en maintenant les sacs dialyseurs à la température de la chambre, dans un courant d'air.

Le dépôt qui se forme au cours de la dialyse n'a pas été séparé, des essais nous ayant démontré qu'il entraînait des enzymes. Une forte agitation du jus précédait donc chaque prise d'échantillon.

Les amylases

Si l'on étudie à 20° C. l'action de 10 ml. de jus dialysé sur 10 ml. d'amidon à 1%, en présence de 10 ml. de tampon à des pH variant de 3.3 à 8.0, on constate que la réaction avec l'iode montre un maximum d'activité à pH 6.5 pour *Ipomoea* et à pH 5.5 pour *Solanum.*

Le pouvoir réducteur cependant indique un maximum d'activité qui se déplace dans les deux cas vers le pH 4.0 au cours de la digestion.

Cette variation du maximum d'activité en fonction du pH dépend aussi de la concentration des enzymes par rapport à l'amidon. Ces constatations dans les jus dialysés de *Solanum* et d'*Ipomoea* nous ont conduits à la recherche des autres glucidases qu'ils pouvaient contenir.

La sucrogène amylase

Après une digestion pendant 72 hr., à 20° C. d'un mélange de 10 ml. d'extrait dialysé, 20 ml. d'amidon à 1%, 10 ml. de tampon à pH 6.5, et 10 ml. d'eau, les ferments sont détruits par ébullition et le milieu est ensuite tamponné à pH 4.5.

Des aliquotes sont additionnées de 1 ml. d'une solution d'invertase; tandis que d'autres reçoivent la même quantité d'invertase bouillie.

Après 12 hr., la différence du pouvoir réducteur exprimé en glucose entre ces deux groupes d'aliquotes est de 4 mg.

Ces essais avec le jus dialysé d'*Ipomoea* et de *Solanum* ont été répétés en remplaçant l'amidon à 1% par une solution dialysée d'amidon à 2%. Les résultats sont analogues. Ils indiquent la formation de sucrose.

L'invertase

Des échantillons de 10 ml. d'une solution de sucrose à 1% et de 10 ml. de tampon à pH 4.5 sont additionnés soit de 10 ml. d'extraits dialysés de *Solanum* et d'*Ipomoea* d'une part, soit de la même quantité des mêmes extraits mais bouillis d'autre part. Après 24 hr. à 20° C., la différence du pouvoir réducteur entre les prises bouillies et non bouillies indique une hydrolyse qui va jusqu'à 75% du sucrose.

La maltase

En plus de la recherche de cette enzyme dans les jus dialysés et tamponnés à pH 6.7 et qui fut négative, nous avons procédé aux expériences suivantes avec des jus obtenus en broyant les patates en présence de toluène et pressant ensuite le tout à travers une toile. Ces jus ont un pH de 4.7 à 4.8.

Nous rapportons l'expérience faite à 25° C. avec *Solanum tuberosum.* Les résultats sont les mêmes avec *Ipomoea Batatas.*

Quatre échantillons de jus frais ont été distribués dans des ballons jaugés de 200 ml.

N° 1: 50 ml. de jus non chauffé et eau diluée à 200 ml.

N° 2: 50 ml. de jus bouilli et eau diluée à 200 ml.

N° 3: 50 ml. de jus bouilli et 100 ml. de maltose (1 mg.) à 200 ml.

N° 4: 50 ml. de jus non chauffé et 100 ml. de maltose (1 mg.) à 200 ml.

Au temps zéro, 25 ml. de chaque échantillon sont pipettés; les N^{os} 1 et 4 sont inactivés par ébullition; tous sont ensuite étendus à 50 ml. Le pouvoir réducteur est déterminé sur 25 ml. et exprimé en millilitres de la solution de thiosulphate *N*/20 nécessaire à la titration en retour. (Méthode Luff et Scholl.)

La même manipulation se répète après 48 hr.: voir le Tableau I.

TABLEAU I

N°	Ml. de $Na_2S_2O_3$, *N*/20	
	Au début	Après 48 hr.
1	19.0	15.6
2	19.0	18.8
3	16.4	16.4
4	16.2	13.0

La différence après 48 hr. entre le N° 2 et le N° 1 est la même qu'entre N° 3 et N° 4; et aussi la même qu'entre N° 4 au début et N° 4 après 48 hr., et qu'entre N° 1 au début et N° 1 après 48 hr.; soit 3.2 à 3.4 cc. Cette différence correspond à l'augmentation du pouvoir réducteur des glucides contenus dans les patates.

La différence au temps zéro, entre N° 2 et N° 3, se retrouve encore après 48 hr.: soit 2.4 à 2.6 cc., et correspond à la quantité de maltose ajoutée (6.25 mg.) dans les prises de dosage. *L'hydrolyse du maltose n'a donc pas lieu.*

Etude des osazones

Pour identifier les glucides des patates sucrées et ordinaires, de même que ceux fournis par l'action des amylases de ces patates sur l'amidon, nous nous sommes servis de la méthode de Fisher des osazones (3, p. 270): 1 partie de sucre, 2 parties de chlorhydrate de phénylhydrazine, 3 parties d'acétate de sodium dans 20 parties d'eau, au bain d'eau bouillante pendant 30 min.

Dans des essais préliminaires nous avons constaté que la forme cristalline des osazones était très variable; cela nous a conduit à faire une étude systématique de la glucosazone, de la maltosazone, et de la cellobiosazone que nous soupçonnions devoir rencontrer.

La glucosazone

Le glucose nous donne à chaud la glucosazone jaune-pâle de forme classique: aiguilles fines réunies en gerbe. C'est celle obtenue directement; nous l'appellerons, glucosazone 1.

Par contre, si l'on filtre la préparation chaude, le filtrat nous donne déjà à 80° C. un précipité jaune-orange en petites boucles plates et courtes ou en forme d'étoile, et qui n'est plus soluble dans l'eau bouillante.

Il est à noter qu'on n'obtient cette forme cristalline qu'après filtration à chaud. Si la préparation est refroidie sans filtration, on ne trouve pas ce produit que nous pouvons appeler: glucosazone 2. Elle est soluble dans l'alcool chaud et garde en cristallisant dans ce solvant sa forme anormale; toutefois, après de nombreuses recristallisations, elle tend à revenir à la forme cristalline classique, et possède toujours le point de fusion de la glucosazone 1: au capillaire: 201 à 202° C., au bloc Maquenne: 228 à 230° C.

De plus si l'on ensemence une solution alcoolique saturée à chaud de glucosazone 2 avec de la glucosazone 1, la cristallisation tend vers la glucosazone 1. Dans les conditions ci-haut mentionnées, le lévulose et le sucrose donnent aussi ces deux formes cristallines d'osazones.

La maltosazone

Ce n'est qu'après refroidissement que nous avons un précipité cristallin abondant. Les cristaux sont en forme d'oursin ou de pelote; ce qui n'est pas du tout la forme cristalline reconnue de la maltosazone.

Recristallisation

Après lavage à l'eau froide, une partie du précipité est dissoute dans l'alcool à 50% bouillant, et l'autre partie dans l'eau bouillante. On constate qu'après deux recristallisations dans l'alcool, la maltosazone a des formes variables qui se rapprochent plus ou moins de la forme cristalline normale généralement reconnue: baguettes plates et striées terminées en fer de lance.

La maltosazone dans l'eau prend et garde, dès la première recristallisation la forme cristalline normale de la maltosazone.

La cellobiosazone

Nous avons opéré parallèlement avec le cellobiose. La cristallisation mère donne des baguettes plates qui ressemblent en tous points à la maltosazone normale. Ce fait nous a tellement frappés que nous avons recommencé l'expérience plusieurs fois pour nous convaincre qu'il n'y avait pas d'erreur dans les préparations.

Comme dans le cas de la maltosazone, la cellobiosazone nous donne par recristallisation dans l'eau des formes normales: aiguilles en oursins. Tandis que dans l'alcool les formes cristallines sont mal définies et se confondent même avec celles de la maltosazone.

Par recristallisation dans l'eau, la cellobiosazone et la maltosazone présentent donc leurs formes normales quel que soit le nombre de purifications. Il n'en est pas de même dans l'alcool.

En dissolvant dans l'eau un mélange de cellobiosazone et de maltosazone, et en laissant cristalliser lentement, on constate qu'elles conservent chacune leur forme classique, tandis qu'en employant l'alcool comme solvant la cristallisation se rapproche plutôt de celle de la cellobiosazone.

Les points de fusion

Les points de fusion de ces osazones après trois purifications, soit dans l'eau, soit dans l'alcool, et dessiccation dans le vide sur le chlorure de calcium sont:

	au bloc Maquenne	Capillaire
Cellobiosazone	218 à 220° C.	196° C.
Maltosazone	198 à 200° C.	183° C.

Les glucides

Dans les patates

Des patates (300 g.) sont râpées, pressées à travers une toile. Le jus, tamponné à pH 3.7 est agité avec 30 ml. de crème d'alumine et mis à la glacière pendant la nuit. Après centrifugation, le liquide est déféqué à l'acétate de plomb, filtré, et concentré dans des sacs de cellophane à 20° C., dans un courant d'air.

La préparation des osazones fournit: (*a*) la glucosazone (point de fusion au capillaire, 201° C.; point de fusion mixte, 201.5° C.) et (*b*) en faible quantité une osazone soluble dans l'eau chaude, que l'on purifie alternativement dans l'alcool et dans l'eau. Suivant les préparations, la forme cristalline est tantôt absente et tantôt se rapproche de celle de la maltosazone; mais le point de fusion varie entre 160 et 170° C. au capillaire. Cette dernière osazone n'est fournie que par l'*Ipomoea*; on ne la trouve pas dans le *Solanum tuberosum*.

Nous avons aussi effectué cette préparation d'osazones avec le liquide de dialyse des macérations faites à la glacière pendant trois jours, soit de poudre de patate, soit de patates râpées. Les résultats sont identiques.

Dans les produits d'hydrolyse

Aux extraits dialysés et concentrés de jus de patates, on additionne 30 ml. d'amidon à 2.5%, tamponnés à pH 6.7. Après digestion à 37° C. pendant quatre jours, la coloration avec l'iode est nulle.

La préparation est alors déféquée au moyen d'acétate de plomb et de crème d'alumine, filtrée et concentrée dans des sacs de cellophane.

Les osazones obtenues sont: (*a*) la glucosazone (point de fusion au capillaire, 202° C.; point de fusion mixte, 201.5° C.) et (*b*) la maltosazone (point de fusion, 183° C.; point de fusion mixte, 183.5° C.) pour la patate sucrée et la patate ordinaire. Si nous nous servons, pour l'hydrolyse de l'amidon, des ferments adsorbés par la crème d'alumine à pH 3.7 et élués à pH 7.0, nous obtenons les mêmes osazones.

Commentaires et conclusions

Les extraits dialysés d'*Ipomoea Batatas* et de *Solanum tuberosum* contiennent des amylases; nous désignons celle qui au cours de l'hydrolyse produit du maltose par "maltogène-amylase", et l'autre qui produit du sucrose par "sucrogène-amylase". Ils contiennent aussi de l'invertase; mais nous n'avons pas réussi à mettre en évidence la maltase, même dans les jus non dialysés.

Dans *Ipomoea Batatas* et *Solanum tuberosum* (à la température de la chambre ou de la glacière), l'action de la sucrogène-amylase est notable, tandis que nous n'avons trouvé aucune trace de l'activité de la maltogène-amylase. Ces patates contiennent de l'amidon, du sucrose, et des sucres réducteurs: sans doute le mélange glucose-lévulose qui constitue le sucre interverti. La présence de maltose n'est pas démontrée.

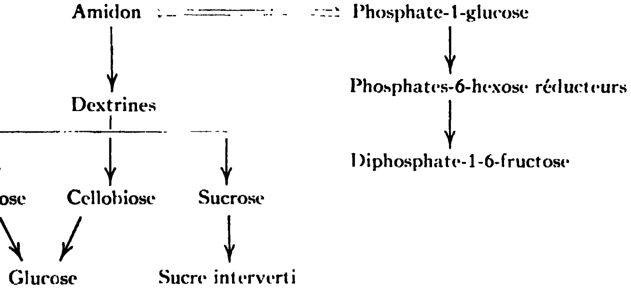
La forme cristalline des osazones conserve son utilité pour l'identification des sucres, pourvu que les conditions de recristallisation soient bien déterminées, par exemple dans l'eau.

L'étude de l'activité amylolytique des jus de patates conduit à toutes sortes de conclusions souvent contradictoires, c'est qu'elle est plus complexe qu'on l'a cru jusqu'à date. Mettant de côté le rôle de la phosphorylase que nous pouvons inactiver par dialyse (8), nous voyons qu'en plus des facteurs: température, pH, temps et concentration, il faut tenir compte des glucidases présentes; surtout si l'on mesure cette activité par le pouvoir réducteur.

L'hydrolyse enzymatique de l'amidon ne donne pas uniquement des dextrines et du maltose: nous avons un exemple avec les jus d'*Ipomoea Batatas* et de *Solanum tuberosum*. Nous sommes en mesure d'affirmer que ce phénomène se retrouve dans les fruits tels que: pommes, bananes, et les feuilles de tabac où il y a aussi formation de sucrose. Ce sucrose, très souvent, se trouve en présence de l'invertase qui l'hydrolyse en proportion plus ou moins grande, suivant les conditions expérimentales. Il nous semble difficile d'admettre la conclusion de Nelson et Auchincloss (10) à savoir que le sucrose provient du fructose ou du glucose, à moins que la formation de ces hexoses dépende de la phosphorylase. Mais nous avons contrôlé que notre dialyse rend cette phosphorylase inactive, et Hanes (8) affirme aussi que le jus de patate est dépourvu des enzymes qui président à la conversion phosphoglucose—phosphoglucomutase et isomérase (11).

De plus, le maltose qui est facilement mis en évidence dans l'hydrolyse de l'amidon par les jus dialysés de patates n'a pas pu être identifié dans les patates. L'absence de maltase rend encore plus incertaine la formation d'hexoses.

Toutes ces raisons nous invitent à reconnaître que le sucrose provient de l'amidon au même titre que le maltose et aussi le cellobiose (1, 2) et nous nous croyons justifiables de développer le schéma de Hanes (8), ce qui peut faciliter l'étude de la constitution de l'amidon.



Bibliographie

1. Bois, E. et Chubb, W. O. Can. J. Research, B, 20(6) : 114-120. 1942.
2. Bois, E. et Nadeau, A. Can. J. Research, B, 16(4) : 114-120. 1938.
3. Browne, C. A. et Zerban, F. W. Sugar analysis. 3rd ed. J. Wiley and Sons, New York. 1941.
4. Doby, G. et Bodnar, J. Biochem. Z. 68 : 191-205. 1915.
5. Giri, K. V. Biochem. Z. 275 : 106-111. 1935.
6. Gore, H. C. J. Biol. Chem. 44(1) : 19-20. 1920.
7. Gore, H. C. Ind. Eng. Chem. 15 : 938-940. 1923.
8. Hanes, C. S. Proc. Roy. Soc. (London) B, 129 : 174-208. 1940.
9. Miyake, K. J. Biol. Chem. 21(2) : 503-506. 1915.
10. Nelson, J. M. et Auchincloss, R. J. Am. Chem. Soc. 55(9) : 3769-3772. 1923.
11. Sutherland, E. W., Colowick, S. P., et Cori, C. F. J. Biol. Chem. 140(1) : 309-310. 1941.
12. Windish, K. et Jetter, W. Z. Spiritusind. 30(50) : 541-542. 1907.
13. Windish, K. et Jetter, W. Z. Spiritusind. 30(51) : 552-555. 1907.

FACTORS IN THE CULTURE MEDIUM THAT AFFECT THE PHOSPHATASE CONTENT OF YEAST[1]

By E. V. Eastcott[2] and J. J. Rae[3]

Abstract

Yeast grown in an inadequately buffered medium may yield a good crop, but the phosphatase content of the yeast obtained is considerably lower than that of yeast grown in a buffered medium. Wide variations in the magnesium concentration of the growth medium have little effect on the phosphatase content of the yeast obtained. Low phosphate concentrations in tomato juice medium result in a yeast with high phosphatase content.

Since a rapid method was available for the determination of phosphatase in yeast (5), it was decided to investigate the effect of certain factors in the culture medium on the phosphatase content of the yeast.

Materials and Methods

Composition of Culture Media

(*a*) *Tomato juice medium.* The culture medium used was, in the main, that suggested by Clark (1) and consisted of:—

(i) *Sugar and salts:*—Dextrose (5 gm.), ammonium nitrate (0.416 gm.), potassium dihydrogen phosphate (0.208 gm., 0.031 *M*), magnesium sulphate heptahydrate (0.104 gm., 0.0084 *M*) and calcium chloride hexahydrate (0.036 gm.);

(ii) *Buffer:*—Citric acid (0.84 gm.), 2 *N* sodium hydroxide (4 cc.) and *N* hydrochloric acid (1 cc.);

(iii) *Filtered tomato juice* (15 cc.).

These constituents were mixed and made up to 45 cc. with water. This produces an adequately buffered medium.

(*b*) *Synthetic medium.* In this medium the concentration of the buffer was changed to:—Citric acid (0.504 gm.), 2 *N* sodium hydroxide (2.4 cc.) and normal hydrochloric acid (0.6 cc.) since less buffer is required than when the acid tomato juice is used, and the filtered tomato juice was replaced by Bios I, inositol (3.4 mg.), Bios IIA, β-alanine (0.017 mg.), *l*-leucine (0.5 mg.), and Bios IIB (15 units). One unit of Bios IIB means that amount, which in excess of all other reagents, in 10 cc. at 25° yields a count of 250 in 24 hr. from an initial count of 1, i.e., 2.5×10^5 cells per cc.

These constituents were mixed and made up to 45 cc. with water. This also produces an adequately buffered medium.

---

[1] *Manuscript received in original form May 4, 1942, and as revised, June 18, 1942. Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*

[2] *Assistant.*

[3] *Lecturer.*

Preparation of Yeast for Analysis

In both cases the culture medium at pH 4.2 was placed in L-shaped rocker tubes, sterilized, and inoculated with 5 cc. of washed yeast suspension (count 10 to 20) (2). Unless otherwise specified the tubes were rocked in a constant temperature bath at 25° for 24 hr. At the end of this time the yeast was centrifuged, washed three times by suspending in water and centrifuging, and dried over calcium chloride in a vacuum desiccator. The yeast was weighed, ground to 40 mesh, and the phosphatase determined by the phenol method (5).

Phosphatase Determinations

(*a*) TOMATO JUICE MEDIUM

1. *Effect of pH*

Yeast may be grown in a buffered solution or in an inadequately buffered solution. The effect of these conditions on the crop and the phosphatase content of the yeast obtained is shown in Table I. The phosphatase values are the average of duplicate or triplicate determinations.

TABLE I

EFFECT OF BUFFERING OF THE GROWTH MEDIUM ON THE PHOSPHATASE CONTENT OF YEAST

Buffering	Yeast used in inoculation	Time, hr.	pH	Crop, mg.	Phosphatase, mg. phenol liberated*
Adequate	H.P.C.	0	4.20	—	4.25
	H.P.C.	16	4.20	90	3.98
	H.P.C.	23.5	3.83	383	4.28
Inadequate	H.P.C.	0	4.26	—	4.03
	H.P.C.	16	4.05	75	3.11
	H.P.C.	24	2.57	340	0.90
Adequate	L.P.C.	0	4.33	--	0.59
	L.P.C.	13	4.32	21	2.96
	L.P.C.	26	4.09	260	3.46
Inadequate	L.P.C.	0	4.30	—	0.59
	L.P.C.	13	4.21	32	2.41
	L.P.C.	26	2.44	390	0.80

* *The phosphatase values are the number of milligrams of phenol liberated from a mixture of 10 mg. of yeast and 10 cc. of 0.01 M disodium phenyl phosphate at pH 4.1 after 20 min. at 37° C. They have been corrected for comparative purposes by means of a standard yeast, which was analysed in each series.*

The yeast obtained in a buffered medium was found to have a high phosphatase content (H.P.C. Yeast); in an inadequately buffered medium, a low phosphatase content (L.P.C. Yeast). When a culture medium was inoculated with H.P.C. yeast and buffered there was little or no decrease in the phosphatase content of the crop; if it was inadequately buffered there was a marked decrease in phosphatase content. When L.P.C. yeast was used in a buffered medium there was an increase in phosphatase; in an inadequately buffered medium there was an increase followed by a decrease. When growth was continued beyond the usual 24 hr. the phosphatase content dropped, and this decrease was more marked in the inadequately buffered media. It was found on investigation that the supernatants of yeasts showing a decrease in phosphatase content did not contain an appreciable proportion of phosphatase. On the basis of these results it was decided to use H.P.C. yeast in a buffered medium in subsequent experiments.

2. *Effect of Magnesium and Phosphate*

The results showing the effects of magnesium and phosphate on the tomato juice medium are given in Table II.

TABLE II

EFFECT OF MAGNESIUM AND PHOSPHATE ON THE PHOSPHATASE CONTENT OF YEAST

Magnesium			Phosphate		
Millimoles Mg added	Crop, mg.	Phosphatase, mg. phenol liberated	Millimoles P added	Crop, mg.	Phosphatase, mg. phenol liberated
8	385	3.79	31	409	4.27
4	301	3.62	8	422	4.38
2	348	3.60	4	406	4.53
1	354	3.34	0	236	7.94
0	288	2.59	—	...	—

Although other workers (4) have shown that magnesium activates phosphatase, it was found that the addition of 0.004 *M* magnesium did not affect the determination of phosphatase in yeast by the phenol method. The sugar and salts reagent contains 8 millimoles of magnesium per litre. When this concentration was reduced by stages to 1 millimole there was no effect on the crop or phosphatase content of the yeast. With no *added* magnesium both crop and phosphatase content were slightly lowered. Filtered tomato juice contains 0.1 mg. of magnesium per cc. This represents a concentration of 1.2 millimoles in the medium.

The sugar and salts reagent contains 31 millimoles of phosphate per litre. When this concentration was reduced by stages to 4 millimoles there was no effect on the crop or the phosphatase content of the yeast obtained. With no *added* phosphate the crop was decreased to about one-half, but the phosphatase content was almost doubled. Filtered tomato juice contains 0.1 mg. phosphate per cc. as determined by King's method (3). This represents a concentration of about 1 millimole in the medium.

In an attempt to investigate further this interesting result a set of experiments was performed in which the phosphate added was reduced gradually from about 4 millimoles to zero. In order to reduce still further the inorganic phosphate it was precipitated from the tomato juice at pH 10 with magnesia mixture. The phosphate was then replaced by equivalent amounts of potassium dihydrogen phosphate and sodium β-glycerophosphate.

TABLE III

EFFECT OF LOW-PHOSPHATE MEDIA ON THE PHOSPHATASE CONTENT OF YEAST

Tube No.	Milligrams of P added		Crop, mg.	Phosphatase, mg. phenol liberated
	In tomato juice	As KH_2PO_4		
1	1.8	36.6	290	3.70
2	1.8	4.6	277	3.68
3	1.8	2.3	254	3.82
4	1.8	1.2	263	4.88
5	1.8	0.6	244	6.03
6	1.8	0	200	6.57
7	0.86	0	44	6.70
8	0.86	0.73	174	7.10

These results confirm the fact that if the phosphorus is lowered, the phospatase content increases. It is impractical however to lower the phosphorus content much below 0.86 because of the small crop obtained. In Tubes 5 and 6 it was observed that 40% of the total phosphorus remained in the yeast centrifugate. The addition of potassium dihydrogen phosphate or of sodium glycerophosphate (data not shown in the table) to the culture medium in amounts sufficient to restore the original concentration of phosphorus in the tomato juice resulted in an increased crop with a similar high phosphatase content.

(*b*) SYNTHETIC MEDIUM EXPERIMENTS

High phosphatase content yeast grown in a buffered synthetic medium at 25° C. for 24 hr. yields a yeast whose phosphatase content is 3.06, a value slightly lower than that obtained with tomato juice medium. The effect of magnesium and phosphate on the phosphatase content of yeast grown in a synthetic medium is shown in Table IV.

TABLE IV

EFFECT OF MAGNESIUM AND PHOSPHATE ON THE PHOSPHATASE CONTENT OF YEAST GROWN IN A SYNTHETIC MEDIUM

Magnesium			Phosphate		
Millimoles Mg added	Crop, mg.	Phosphatase, mg. phenol liberated	Millimoles P added	Crop, mg.	Phosphatase, mg. phenol liberated
8	161	3.14	31	135	2.34
1	160	3.07	12	130	1.81
0.5	153	3.35	8	102	2.64
0	No growth	—	4	65	2.47
			0	No growth	—

When the magnesium concentration of the sugar and salts reagent was reduced by stages to 0.5 millimoles there was no effect on the crop or its phosphatase content. With no added magnesium there was no crop. When the phosphate concentration was reduced to 4 millimoles the crop was reduced to one-half while the phosphatase content remained about the same. With no added phosphate there was no crop. The Bios IIB used contained no phosphorus.

References

1. Clark, N. A. J. Phys. Chem. 26 : 42-60. 1922.
2. Fraser, C. G. J. Phys. Chem. 25 : 1-9. 1921.
3. King, E. J. Biochem. J. 26 : 292-297. 1932.
4. Myrbäck, K. Ann. Rev. Biochem. 8 : 59-80. 1939.
5. Rae, J. J. and Eastcott, E. V. J. Biol. Chem. 136 (2) : 443-447. 1940.

THE SYSTEM ETHANOL-METHANOL AT 40° C.[1]

By A. C. Morris[2], L. T. Munn[2], and G. Anderson[2]

Abstract

The system ethanol-methanol was studied at 40° C. using the original and also a modified form of the apparatus of Ferguson and Funnell. The total pressure curve is linear and the partial pressure curves agree with Raoult's law within the experimental error.

Introduction

The system ethanol-methanol has been studied by Schmidt (9) at 40° C., and his total pressure curve indicates that there is a slight positive deviation from ideality. Unfortunately his value for the vapour pressure of pure methanol is well below that of other investigators, and because of this fact the extent of the deviation from Raoult's law is still in doubt. A study of this system was undertaken by the authors in order to clear up this point, and also in order to test an improved form of the apparatus of Ferguson and Funnell (3).

Materials

Anhydrous alcohols of reagent quality were dried either by distillation over sodium or by the Lund-Bjerrum method (7).

Experimental Method

Morris used the earlier type of apparatus (2) in which the vapour was circulated over the liquid phase until equilibrium was attained, and a known part of the vapour was then condensed and weighed. The vapour was analysed by means of vapour density measurements, the proper constants being determined experimentally. The composition of the liquid phase was obtained by difference from the amounts of the alcohols initially taken and the amounts that were recovered in the vapour phase.

The apparatus was later modified in order to eliminate the use of mercury traps and to avoid possible errors that might arise from the condensation of mercury in the vapour-phase part of the apparatus. The new form is shown in Fig. 1. Like the older type it was constructed of Pyrex glass. Known weights of the alcohols were placed in the sample tube *A* through the straight tube which was then sealed. The sample tube was connected to the apparatus by means of the ground glass joint *B*. The sample was freed of dissolved air by freezing it in liquid air, evacuating, closing the stopcock on the sample tube, and allowing the tube to warm up to room temperature, and then repeating the whole operation several times. It was distilled into the tube *C* by cooling the latter in liquid air and opening the stopcock, the line to the vacuum pump being closed after the final evacuation. When the distillation

---

[1] *Manuscript received in original form May 4, 1942, and as revised, July 7, 1942. Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*

[2] *Student working under the direction of Prof. J. B. Ferguson.*

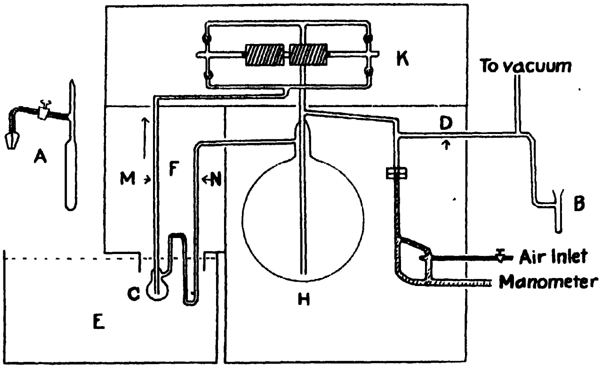


FIG. 1. *The modified form of the Ferguson–Funnell apparatus.*

was complete, the system was sealed off at the point *D*. The bath *E* was then filled with water and maintained at 40° C. ± 0.01° C. The air-baths *F*, *H*, and *K* were kept at 45, 44, and 50° C., respectively, and the temperature of *H* was maintained within ± 0.1° C. The temperatures were read on mercury thermometers that had been compared with a recently calibrated platinum resistance thermometer which was accurate to better than 0.02° C. Bath *F* was so designed that glass seals could easily be made at the points *M* and *N* at the conclusion of the experiment without undue thermal disturbance of the vapour phase. Bath *K* contained the Funnell–Hoover gas pump (4). Copper sheeting extended from the air-bath *F* well below the water level in *E*. The vapour was circulated over the liquid phase until the pressure became constant, usually a matter of several hours. The bulb *C* was then sealed off. It was dried externally, weighed, opened, dried internally using a slow current of dry air, and then reweighed. The weight of the liquid phase was obtained from the weight difference by correcting it for air buoyancy and for the vapour that was present. The latter correction amounted to approximately 0.5% of the vapour, since the large bulb had a volume of five litres.

The new apparatus and procedure differs from the original in that the sample is now distilled directly into the vapour pressure bulb *C*; the weight of the liquid phase is determined experimentally; no vapour is condensed; and the mercury traps are eliminated. The composition of the liquid phase is obtained from a total pressure curve, and the composition of the vapour phase is found by difference between the original amounts of the alcohols taken and the amounts recovered in the liquid phase. In the former procedure the recovery was obtained from the vapour phase. The mercury-in-glass manometer was sealed to, and was a part of, the all-glass apparatus in both cases.

The apparatus was also used by Munn and Anderson for total pressure measurements but the gas space was reduced by the elimination of the large bulb and the gas circulating pump. A small vapour phase was especially desirable in the case of the solutions.

Total and Partial Pressures

The total and partial pressure results are given in Table I and are shown in Fig. 2. Munn's values for the vapour pressures of the pure alcohols were used in drawing the total pressure curve. Had the value of Morris for methanol been used, the partial pressures of the latter would have approached more closely the Raoult law line. It should be noted that the total pressures of Morris are independent measurements obtained at the same time that the compositions of the phases were determined.

TABLE I

THE TOTAL AND PARTIAL PRESSURES FOR THE SYSTEM ETHANOL-METHANOL AT 40° C.

Mole per cent methanol		Total pressure, P	Ethanol $\frac{n_1}{n_1 + n_2}p$	Methanol $\frac{n_2}{n_1 + n_2}p$	Observer
Liquid	Vapour				
0	0	135.2	135.2	0	Munn and Anderson
0	0	135.4	135.4	0	Morris
0	0	134.8	134.8	0	Schmidt
14.4	25.2	152.8	114.3	38.5	Morris
26.3	41.0	166.0	97.9	68.1	Morris
31.5		174.6			Munn and Anderson
47.0	64.4	195.0	69.4	125.6	Munn and Anderson
50.2		198.8			Munn and Anderson
65.2		217.6			Munn and Anderson
73.2	84.6	228.5	35.1	193.4	Munn and Anderson
82.7	89.4	238.5	25.4	213.1	Morris
86.0		245.3			Munn and Anderson
89.7	93.3	249.0	16.7	232.3	Morris
100	100	262.6		262.6	Munn and Anderson
100	100	261.5		261.5	Morris
100	100	257.4		257.4	Schmidt

The vapour pressures obtained for ethanol are in agreement with the I.C.T. value of 135.3 mm. (6, p. 217). There is no such agreement between the results of the various investigators in the case of methanol. Schmidt's value is certainly too low. Other values are: (i) Young (11) 260.5; (ii) Ferguson and Funnell (3) 261.7; (iii) Wrewsky (10) 261.9; and (iv) Bredig and Bayer (1) 262.8 mm. Values (ii) and (iii) were extrapolated from 39.90° and value (iv) from 39.76°. The discrepancies are much greater than would be expected, since the greatest care was exercised by these investigators. Without doubt, they are due in part to the presence of water in the alcohol but also in part to other impurities. Munn dried two samples of alcohol by the same method and the densities of the final products were D_4^{25}, 0.7866 and 0.7865 respectively. Gibson's value (5) is 0.78655. The vapour pressures were 262.6 and 265.3 mm. The latter value was checked by the value

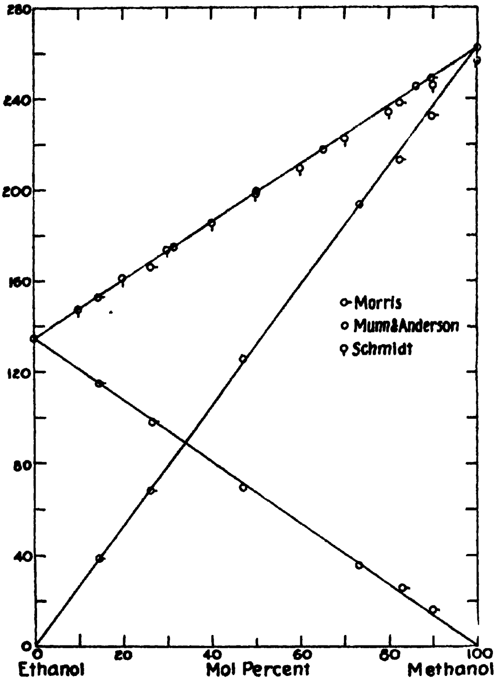


FIG. 2. *The partial and total pressures for the system ethanol–methanol at 40° C.*

265.6 obtained for a sample of synthetic alcohol that was said to be very pure but not sold as a reagent chemical. Evidently the density is not a sufficient criterion of purity, although in general use for this purpose. The usual chemical tests also do not seem to be satisfactory since the various workers tested their alcohols.

Since the partial pressure curves indicate that the system closely approaches an ideal one, the deviation from ideality of one alcohol must be matched by the deviation on the part of the other alcohol. If we assume an equation of state for the vapour of the type $P\ (V\text{-}\beta) = RT$, the values of β may be calculated by means of the equation of Scatchard and Raymond (8). These, in turn, yield formula-weight deviations from the theoretical values, of 0.7 and 1.1% for ethanol and methanol respectively. This gives an approximate idea of the contribution of the vapour to the deviations. The experimental vapour densities as determined in this laboratory agree very well with those so calculated for ethanol and acetone, but those for methanol are invariably much higher. The writers hesitate to accept as final, formula-weight values for methanol as low as 32.4 at 50° C., and these investigations are being continued. The theoretical values were used in calculating the mole percentages given in the table.

References

1. BREDIG, G. and BAYER, R. Z. physik. Chem. 130 : 1-14. 1927.
2. FERGUSON, J. B., FREED, M., and MORRIS, A. C. J. Phys. Chem. 37 : 87-91. 1933.
3. FERGUSON, J. B. and FUNNELL, W. S. J. Phys. Chem. 33 : 1-8. 1929.
4. FUNNELL, W. S. and HOOVER, G. I. J. Phys. Chem. 31 : 1099-1100. 1927.
5. GIBSON, R. E. J. Am. Chem. Soc. 57 (9) : 1551-1557. 1935.
6. INTERNATIONAL CRITICAL TABLES. Vol. 3. McGraw-Hill Book Company, Inc., New York and London. 1928.
7. LUND, H. and BJERRUM, J. Ber. 64B : 210-213. 1931.
8. SCATCHARD, G. and RAYMOND, C. L. J. Am. Chem. Soc. 60 (6) : 1278-1287. 1938.
9. SCHMIDT, G. C. Z. physik. Chem. 121 : 221-253. 1926.
10. WREWSKY, M. Z. physik. Chem. 81 : 1-29. 1912-13.
11. YOUNG, S. Sci. Proc. Roy. Dublin Soc. 12 : 374-443. 1909-10.

THE SYNERESIS OF SILICA GELS CONTAINING ADDITION AGENTS[1]

BY L. A. MUNRO[2] AND G. E. MONTEITH[3]

Abstract

The effect of addition agents on syneresis of silica gel is reviewed. Various methods of measurement of syneresis have been investigated and a convenient method that gave duplicate results agreeing within 1.2% is described. The effect of a series of alcohols—methyl, ethyl, glycol, glycerol, and erythritol—on syneresis has been studied. The results indicate that the total volume of syneretic liquid at equilibrium was the same as that of the control (within the experimental error) and that no adsorption had taken place in the gel itself. The data on the adsorption of the alcohols was determined by analysis of the syneretic liquid for its alcohol concentration by an oxidation method using chromic acid.

Introduction

The effects of various neutral organic addition agents on the time of set of silica gels have been shown to be widely divergent for alkaline gels (12, 13). In a study using a series of monohydric and polyhydric alcohols it was noted that when the system was acidic all the alcohols acted as retarders of gelation. In the alkaline range the monohydric alcohols and glycol were accelerators. At pH 7 all had a uniform and retarding effect; this eliminated therefore the dielectric constant of the addition agent as the principal factor in determining gelation. If the specific effects observed on the alkaline gels are to be explained by differences in sorption of the addition agents or in the solvation of the micelles during gelation, this should be indicated by the composition of the syneretic fluid. The work described below was undertaken to investigate this, using as addition agents the series of alcohols studied in the experiments on the time of set.

The work on syneresis and the theories concerning it advanced up to 1929 have been reviewed by Kuhn* (8). Evidently considering the gelation phenomenon to cover the life history of a gel until an equilibrium is finally reached, Kuhn depicts syneresis as a continuation of the disintegration process following setting by structural changes and desolvation. A perusal of Kuhn's paper will show the great differences in behaviour of different types of gels; for example, rubber, silicic acid, and viscose give increasing amounts of syneresis with increasing concentration of gel, whereas the opposite behaviour is reported for starch, agar, cellulose acetate, and dyestuffs.

---

* *One important part of Kuhn's paper, viz., a discussion of Liepatoff's work is in error owing to certain mistakes of translation and interpretation. See Liepatoff (10).*

[1] *Manuscript received in original form April 28, 1942, and as revised, August 5, 1942. Contribution from the Department of Chemistry, Queen's University, Kingston, Ont.*

[2] *Associate Professor of Chemistry.*

[3] *Graduate Research Assistant, 1941. At present, Chemist, Canadian Industries Ltd. Montreal, Que.*

Syneresis of silica gels has been reported by several investigators, but the results and conclusions are not always in agreement. This may be due partly to different methods of measurement, and partly to the neglect of such factors as pH, temperature control, and total surface per cubic centimetre. Fracture of the gel or mechanical disturbance causes differences in the rate and amount of syneresis.

The effect of addition agents on syneresis has been recorded in only a few cases. Rossi and Marescotti (16, 17), Rossi and Scandellari (18), and Jirgensons (7) have noted the effect of electrolytes on agar, starch, and albumin gels.

The effect of electrolytes on syneresis has been noted for various inorganic gels by Prakash and Dhar (14).

Bonnell (2) studied the effect of neutral salts on silica gel syneresis. The work was done at a pH of 6.5 and at 20° C. The added salts increase the rate and final volume of syneresis up to a maximum which appears to be between 0 and 1.353% in the case of potassium chloride at a silica concentration of 8.4%. It was found that potassium salts are more potent than sodium salts and the sulphates better than the chlorides.

Hardy (4), using azomethine, observed that, in an ether gel, syneresis occurs in a few minutes, in absolute alcohol in a day, and in aldehyde in a few hours. Slight additions of water retard syneresis from an hour to a day. Alcohol added to a gel containing salt gives increasing syneresis in a short period of time, but the end-point is the same as for gels containing electrolyte alone. The effect of organic addition agents on syneresis of silica gel has apparently escaped attention.

Experimental

A comparison of three methods of measurement was first undertaken. In Method 1 the apparatus described by Ferguson and Applebey was used (3). This consisted of a cylinder of 50 cc. capacity having a graduated neck made from an old burette. The bottom of the cylinder was connected to a reservoir bulb. It is labelled No. 1 in Fig. 1. In this method a standard volume of

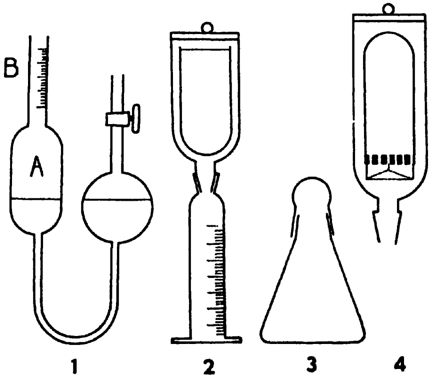


FIG. 1. *Types of apparatus used in the different studies.*

gel is formed in Tube *A* on a platform of carbon tetrachloride. The syneretticum is measured by raising the level of the carbon tetrachloride and reading the volume of liquid displaced into the graduated tube, *B*.

The second method made use of a simplification of the apparatus described by Bonnell (1) (No. 2, Fig. 1). The gel was formed in a vaselined extraction thimble and as soon as it had set it was transferred to the experimental one, saturated with syneretic liquid from a similar gel.

In the third method, uniform Erlenmeyers having the same internal surface were coated with wax. When the gel had synerized, the flask was inverted and the volume of liquid measured at different times.

A comparison of the results for a 1.65% silicate gel (made from 25 cc. of silicate, containing 1.65% silica, and 25 cc. of acetic acid) at pH 11.0 and 20° C. is shown in Fig. 2. These curves represent the mean of several readings.

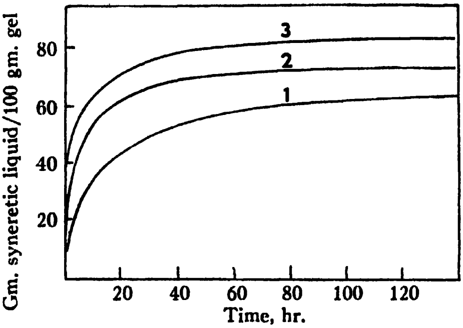


FIG. 2. *Syneresis curves obtained by different methods: Curve 1—Ferguson and Applebey method. Curve 2—Bonnell wetted cone or thimble method. Curve 3—Waxed Erlenmeyer method.*

Factors Contributing to Experimental Differences

Holmes *et al.* (6) found that the amount of syneresis per cubic centimetre varied with the surface. Ferguson and Applebey (3) found that the same volume of gel in containers of different shapes, viz., a sphere, cylinder, cone, and cuboid, gave a maximum difference of 6% in the volume of liquid, although the surface area varied as much as 35%. It is indeed probable that the volumes of syneretic liquid are within the experimental error. The differences *herein* noted must therefore be due to other factors inherent in the three methods. The gel used in these experiments was more dilute and differences in height of the gel and thus in compression may be of more importance.

Kuhn states, "Mechanical influences affect very strongly the spontaneous exudation of liquid from gels. If a gel which shows no noticeable syneresis is subjected to the slightest pressure it loses liquid; for example, soaps (aqueous alcohol and glycerine)." Meyer (11) has described similar observations with starch. A 5% starch gel which was stored away quietly for two months exuded 1 cc. of liquid; a similar gel, however, after 48 hr. during which it was given an occasional feeble shake had exuded liquid, and after seven days 6 cc. of liquid was freed. A 6% gel had exuded no liquid after eight days of quiet standing; when a rod, held upright in the gel, was moved slightly, however, the gel was torn, and it collapsed. The 'fluid' produced by this mechanical disintegration is not due to syneresis, but, partly at least, to thixotropic unsettling.

Further methods for the measurement of syneresis were tried and every precaution was taken to achieve similarity of conditions. First, the gel itself was allowed to synerize in a waxed seamless Whatman extraction thimble, 80 mm. high and 22 mm. in diameter, with a hemispherical bottom. The container was saturated by boiling it in wax for one hour, and then allowing it to cool. This expelled nearly all the trapped air. The cone was then dipped twice in warmed wax and a uniform coating was thus formed. A hole 2.5 mm. in diameter was punched in the centre of the bottom of the thimble, and after the final dipping this was reamed out to a diameter of 2.0 mm.

When the apparatus was about to be used, a circular piece of drafting-tape was sealed over the hole in the cone or thimble by means of a thin coating of wax. The sol was then pipetted into the thimble and allowed to set. The piece of drafting tape was then removed, the thimble placed in the apparatus and the syneretic liquid collected in the graduated cylinder (No. 2, Fig. 1).

Results with this apparatus were not very satisfactory, particularly with acid gels. Data for alkaline gels from '3.35% silica' silicate obtained by J. A. Pearce in this laboratory at pH 10.5 are given in Table I. Gelating mixture (50 cc.) was prepared as described previously and 10 cc. of the mixture pipetted into the waxed thimble. The time was measured from the instant of mixing.

A further modification illustrated as No. 4, Fig. 1, was then tried. Wax discs, 0.5 to 2.0 mm. thick, were cast to fit the extraction thimble. These

TABLE I

DATA OBTAINED WITH '3.35% SILICA' GELS, AT 20° C., pH 10.5

Addition agent	Hours				
	23	44	69	118	163
	Volume of syneretic liquid, cc.				
Control	8.3	8.5	8.5	8.5	8.6
	8.3	8.3	8.5	8.7	8.7
Glycol, 3 cc.	8.5	8.8	8.9	9.0	9.0
	8.5	8.8	8.8	8.8	8.9
Glycerol, 3 cc.	8.8	9.0	9.0	9.0	9.0
	8.4	8.7	8.7	8.8	8.8
Erythritol*, 4 gm.	8.8	9.0	9.0	9.0	9.0
Mannitol, 4 gm.	8.0	8.1	8.3	8.3	8.3
	7.9	8.1	8.3	8.3	8.3

* *In the case of the second sample, some silica came through and precipitated on the bottom of the graduate.*

discs were pierced uniformly with 15 holes 1 mm. in diameter. When the gel mixture had been pipetted into the thimble the disc was inserted in the top and sealed on by means of a hot knife-blade. As soon as the gel had set, the container was inverted and the hole in the bottom opened to act as an air vent. The inverted thimble was supported on three glass points. This apparatus gave the most consistent results.

Syneresis was virtually complete after 20 days, whereas with the other apparatus syneresis was still proceeding after 90 days. The total volume of syneresis was also greater with this method, and the final volumes checked fairly well.

However, near the end of the syneresis period the holes have a tendency to plug up, possibly owing to secondary gelation. This factor may cause differences in the final volumes of duplicate samples. The other possibility is that the syneretic liquid cannot escape with the same ease from all the thimbles.

Preparation of the Sol

In these experiments, Baker's Crystalline silicate and freshly distilled water were used. The silicate had a specific gravity of 1.050 at 20° C., and it contained 2.5% of SiO_2. The acid solution was prepared by adding 50.0 cc. of glacial acetic acid to distilled water and making up to 500 cc., giving a normality of 1.63.

To obtain consistent results the method of mixing is important. The silicate solution is always added to the acid solution. The required amount of acid is measured from a burette and made up to 25 cc. with water or addition agent plus water. Silicate solution (25 cc.) is then added with stirring for five seconds. When crystalline alcohols were added, the weighed amount was dissolved in the acid and the volume of the mixture made up to 50 cc.

Ferguson and Applebey (3) have shown that temperature has a marked effect on syneresis, a 10° rise increasing the amount about 1.8 times. Bonnell verified this, using hydrochloric acid and acetic acid as coagulants.

Since there is, owing to the heat of mixing, a definite rise in temperature that might influence the syneresis, the separate silicate and acid solutions were kept at a temperature below that of the bath (25° C.) containing the apparatus. The correct premixing temperature for gels of pH 10.4 was found to be 22.3° C.; for gels of pH 9.4, 21.7° C.; and for gels of pH 7.4, 21.6° C.

To check the similarity of these gels with those previously studied, times of set were determined, as previously described, with the residual mixture after removal of the pipetted sample for the syneresis experiment. The gel concentration used was much lower than concentrations used by other experimenters in this field. At this dilution, gels never set in less than five minutes, which is ample time for the necessary manipulation.

The tubes were placed in an air thermostat regulated to 25° C., within 0.05° C., by means of a sensitive mercury-toluene thermoregulator operating a 40 watt lamp. A small fan revolved behind the lamp. The motor and shaft of the fan were mounted on a nearby table so as to avoid any vibration of the fragile gel.

Relation of pH and Syneresis

The change in pH of a gel on setting has already been noted (12). Several investigators have recorded the influence of pH on syneretic volume for silica gels. Kuhn (8) states that neutral gels showed weak syneresis, whereas basic gels which set rapidly, synerize quickly. Ferguson and Applebey showed that whereas acid gels (without addition agents) synerize more slowly, the final quantity of synereticum is greater than with alkaline gels.

However, the pH at which syneresis is a minimum depends on the concentration of the gel. Bonnell, using concentrated gels containing 6.5 to 8.8% silica, showed that the volume of liquid synerized passes through a minimum at about pH 8.5, increasing steeply beyond 10. Ferguson and Applebey, using a 3.87% silica gel and pH 5, 7, 9, and 10 found the smallest volume at pH 10. They observed that at pH 4 to 5 more concentrated gels gave greater syneresis. It has been shown (12) that the pH at which the time of set is a minimum depends on the concentration of the gel, varying from pH 7.5 to pH 10 as the percentage of silica was increased. The discrepancies between Bonnell's and Ferguson and Applebey's results may be due to the concentration factor.

In the present studies both the glass electrode and indicators were used. It was found advisable to have a standard solution to check the glass electrode, as in the strongly alkaline range it gives somewhat erroneous results. Check values for the two methods varied less than 0.1 pH unit.

It is noted that the gel becomes much more alkaline during the period between the time of mixing and that of the setting of the gel. A number of gelating mixtures of pH 9.0 gave, on setting, gels of pH 9.6 to 9.7. The liquid exuded by syneresis was withdrawn every 12 hr. and its pH recorded. The synerized liquid was of a constant pH, throughout the whole period of syneresis, as recorded by the Coleman glass electrode.

Analysis of Syneretic Liquid

The syneretic liquid was analysed to determine whether the gel adsorbed any of the alcohol while setting, and to study the further processes taking place during syneresis.

The oxidation method essentially similar to that given for glycerol in Lawrie's book "Glycerol and the glycols" (9, p. 238) was employed. This is based on Hehner's method (5). A standard concentrated solution of chromic acid (79.86 gm. of potassium dichromate and 200 cc. of concentrated sulphuric acid per litre) was used to oxidize the different alcohols, the excess dichromate being titrated with ferrous ammonium sulphate. Twenty-five cc. of ferrous ammonium sulphate was equivalent to 10 cc. of chromic acid solution. From 50 to 100% excess chromic acid was measured out accurately in duplicate into 250 cc. Erlenmeyer flasks (approximately 40.0 cc. for erythritol and 20 cc. for methyl alcohol). Five cc. of the syneretic liquid was then pipetted into the flask, which was quickly placed under a reflux condenser to avoid loss of the lower alcohols by evaporation. A volume of concentrated sulphuric acid equal to the chromic acid solution was then added slowly down the reflux condenser. The heat generated starts the reaction vigorously. The flask was finally heated over a boiling water-bath for ½ hour to insure completion of the reaction. The flask was then cooled and the contents titrated with ferrous ammonium sulphate, 0.1% potassium ferricyanide solution being used as an outside indicator.

Richardson and Jaffé (15) found that by increasing the amount of sulphuric acid added, the time of boiling (two hours at least was recommended by Hehner and Lawrie) could be greatly reduced. The writers have found one-half hour to be ample. As can be seen from the equations, large quantities of sulphuric acid enter into the reaction.

Reactions with $K_2Cr_2O_7$. *Potassium dichromate. Mol. wt. 294.22*

Methyl alcohol. CH_3OH – 32.0

$$3\ CH_3OH + 2\ K_2Cr_2O_7 + 4\ H_2SO_4 \longrightarrow CO_2 + 6\ H_2O + Cr_2(SO_4)_3 + K_2SO_4$$

Ethyl alcohol. C_2H_5OH – 46.0

$$3C_2H_5OH + 2\ K_2Cr_2O_7 + 8\ H_2SO_4 \longrightarrow 3\ CH_3COOH + 11\ H_2O + 2\ Cr_2(SO_4)_3 + 2\ K_2SO_4$$

Ethylene Glycol – 62.0

$$3\ C_2H_4(OH)_2 + 5\ K_2Cr_2O_7 + 20\ H_2SO_4 \longrightarrow 6\ CO_2 + 29\ H_2O + 5\ Cr_2(SO_4)_3 + 5\ K_2SO_4$$

Glycerol – 92.08

$$3\ C_3H_5(OH)_3 + 7\ K_2Cr_2O_7 + 28\ H_2SO_4 \longrightarrow 9\ CO_2 + 40\ H_2O + 7\ Cr_2(SO_4)_3 + 7\ K_2SO_4$$

Erythitol – 122.08

$$C_4H_6(OH)_4 + 3\ K_2Cr_2O_7 + 12\ H_2SO_4 \longrightarrow 4\ CO_2 + 3\ Cr_2(SO_4)_3 + 3\ K_2SO_4 + 17\ H_2O$$

It is noted that all the above alcohols are oxidized completely to carbon dioxide, except ethyl alcohol, which is oxidized to acetic acid.

Tabulation of Results

The results are given in Table II. In Column 4 are given the average volumes of syneretic liquid from the duplicate experiments, the extent of deviation between Tubes I and II being shown. With this type of apparatus the maximum deviation between duplicates was ± 0.3 cc. or 1.2%, while the variation from the value for the control was ± 0.5 cc. or 2.9%. The slight variations observed in pH apparently did not affect the results. In a second control gel of pH 8.0 the syneresis was approximately 5 cc. per 100 gm. less than the control at pH 9.7.

In the last two columns are given the amount of addition agent in the syneretic liquid and in the original gelation mixture. Very good agreement was obtained between duplicate titrations and between duplicate experiments (Tubes I and II) except in the case of methyl alcohol and Tube II of erythritol.

TABLE II

Data obtained with '2.5% silica' gel at 25° C, pH 9.7, using improved apparatus (No.4)

	pH		Volume of syneretic liquid from 25 cc. of gel	Volume as cc./100	Addition agent	
	At set	Of syneretic liquid			Gm./100 cc. syneretic liquid	Gm./100 cc. original mixture
Control	9.7	9.7	17.4 ± 0.0	69.6	0	0
Methyl alcohol	9.7	9.8	17.3 ± 0.3	69.2	1.57	1.60
Ethyl alcohol	9.7	9.85	17.9 ± 0.1	71.6	2.30	2.30
Glycol	9.7	9.7	16.8 ± 0.2	67.2	3.12	3.12
Glycerol	9.7	9.7	17.4 ± 0.0	69.6	4.52	4.52
Erythritol	9.7	9.7	17.9 ± 0.1	71.6	6.10 5.93	6.10
Control	7.9	8.0	16.1 ± 0.1	64.4	—	—

Two typical examples that show the accuracy of the method are given below.

Example Titrations

Ethyl alcohol, 2.302 gm. per 100 cc. Sample of synereticum, 5 cc.

From Tube I *(a)* 15.00 cc. of dichromate required *(a)* 22.20 cc., *(b)* 22.30 cc. ferrous ammonium sulphate = 0.1150 gm., 0.1145 gm. ethyl alcohol.

From Tube II *(c)* 15.00 cc. dichromate required 22.25 cc., 22.10 cc. ferrous ammonium sulphate = 0.1147 gm., 0.1152 gm. ethyl alcohol or 2.297 gm. per 100 cc.

Glycol, 3.120 gm. per 100 cc.

5 cc. from Tube I, using 25.00 cc. dichromate, required 23.90, 23.90cc.
Tube II, using 25.00 cc. dichromate required 23.90, 23.80 cc.
= 0.1560 gm. of glycol or 3.120 gm. per 100 cc.

The ethylene glycol used was 97.1% pure and the glycerol was 94.2% pure. This degree of purity is quite normal as it is difficult to remove the last traces of water from these alcohols.

It will be seen from the analysis of the syneretic liquid given above that no selective adsorption of the alcohols has taken place. The syneretic liquids all contained silica in undetermined amounts.

It appears that the specific effect of these addition agents on the time of set and the gelation process is not indicated by the composition of the syneretic fluid.

References

1. Bonnell, D. G. R. Trans. Faraday Soc. 28 : 1-11. 1932.
2. Bonnell, D. G. R. Trans. Faraday Soc. 29 : 1221-1226. 1933.
3. Ferguson, J. and Applebey, M. P. Trans. Faraday Soc. 26 : 642-655. 1930.
4. Hardy, W. B. Proc. Roy. Soc. (London) A, 87 : 29-37. 1912.
5. Hehner, O. J. Soc. Chem. Ind. 4 : 9-11. 1889.
6. Holmes, H. N., Kaufmann, W. E., and Nicholas, H. O. J. Am. Chem. Soc. 41 (9) : 1329-1336. 1919.
7. Jirgensons, B. Kolloid-Z. 74 : 300-305. 1936. (Chem. Abstracts, 30 (15) : 5096. 1936.)
8. Kuhn, A. Kolloid-Z. 46 : 299-314. 1928.
9. Lawrie, J. W. Glycerol and the glycols. The Chemical Catalog Company, Inc., New York. 1928.
10. Liepatoff, S. Kolloid-Z. 48 : 62-63. 1929.
11. Meyer, A. Kolloidchem.-Beihefte, 5 : 1-48. 1913.
12. Munro, L. A. and Pearce, J. A. Can. J. Research, B, 17 : 266-280; 404-408. 1939.
13. Munro, L. A. and Pearce, J. A. J. Phys. Chem. 44 : 1024-1033. 1940.
14. Prakash, S. and Dhar, N. R. J. Indian Chem. Soc. 7 : 417-434. 1930.
15. Richardson, F. W. and Jaffé, A. J. Soc. Chem. Ind. 17 : 330-333. 1898.
16. Rossi, G. and Marescotti, A. Gazz. chim. ital. 63 : 121-127. 1933. (Chem. Abstracts, 27 (15) : 3653. 1933.)
17. Rossi, G. and Marescotti, A. Gazz. chim. ital. 66 : 223-227. 1936. (Chem. Abstracts, 31 (4) : 926. 1937.)
18. Rossi, G. and Scandellari, G. Gazz. chim. ital. 66 : 459-464. 1936. (Chem. Abstracts, 31 (11) : 3762. 1937.)

THE HYDROLYSIS OF ALIPHATIC NITRILES IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS[1]

By B. S. Rabinovitch[2] and C. A. Winkler[3]

Abstract

Studies of nitrile hydrolysis in concentrated acid media have been extended to the hydrolysis of hydrocyanic acid, acetonitrile, and cyanoacetic acid in hydrochloric acid solutions of concentration 1 to 8.5 *N*. It appears that the hydrolysis of aliphatic nitriles in concentrated sulphuric and hydrochloric acids provides systems of consecutive, irreversible unimolecular reactions over the complete range $k_{nitrile} \ll k_{amide}$ (more dilute acid) to $k_{nitrile} \gg k_{amide}$ (highly concentrated acid), for a sufficient range of acid concentrations. The limit, $k_{nitrile} \gg k_{amide}$, is not attained in hydrobromic acid solutions. The nitriles studied here exhibit a large decrease in activation energy with increase of acid concentration, similar to that observed earlier for propionitrile. The magnitude of the variation of the Arrhenius parameters is specific for each nitrile. For the acetonitrile hydrolysis, the increase in rate with increase of acid concentration largely follows the accompanying activation energy decrease. The relative rates of hydrolysis of different nitriles, at given acid concentration, are not governed by differences in activation energy. The variation of activation energy is briefly discussed in relation to certain other factors.

Introduction

It was found in a previous investigation (16) that the activation energy for the hydrolysis of propionitrile in concentrated hydrochloric acid solutions decreases by 6.7 Cal. with increase of acid concentration from 1 to 10 *N*. The very rapid increase in rate observed in this concentration range is largely accounted for by the decrease in activation energy. This behaviour was found to be general for the reaction in concentrated mineral acid solutions (13).

The study of propionitrile has also shown that at higher acid concentrations (above 4 *N*), it cannot be assumed, as other investigators have done (8), that the rate of hydrolysis is independent of the hydrolysis of the intermediate amide. Consequently, the reaction rate should not be measured by determination of ammonia alone, but by analysis for total amide and ammonia. It was found that the reactions, propionitrile + $H_2O \xrightarrow{k_1}$ propionamide + $H_2O \xrightarrow{k_2}$ propionic acid + ammonia, constitute a system of consecutive, irreversible, unimolecular reactions for which the ratio, $k_1 : k_2$, varies with the catalyst and its concentration. For hydrochloric and sulphuric acids, variation of the rate ratio over the complete range, $k_1 \ll k_2$ (1 *M* acid) to $k_1 \gg k_2$ (above 11 *M* acid), was observed.

The study has been extended here to include the hydrolysis of acetonitrile and hydrocyanic and cyanoacetic acids in hydrochloric acid solutions. This has permitted a more general examination of the correlation between increase in rate of hydrolysis with increasing acid concentration and variation of the

---

[1] *Manuscript received in original form February 4, 1942, and as revised, May 11, 1942. Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.*

[2] *Postgraduate Student, and holder of a Studentship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry.*

Arrhenius parameters. Since the structure and characteristics of the nitriles employed vary considerably, it was expected that variation of activation energy with acid concentration would be specific. It was of particular interest to determine whether E varies in the hydrocyanic acid hydrolysis, as the increase of rate with hydrochloric acid concentration for this nitrile has been related by other workers (9) to the square of the mean ion activity of the acid.

Experimental

Acetonitrile was obtained commercially and was purified by distillation to a boiling range of 0.1° C.

Hydrocyanic was prepared by a standard method (20), and was further purified by repeated distillation between two traps, the first and last fractions being rejected. Aqueous solutions were stabilized by addition of a drop of dilute acid (12) and were stored in an ice-box.

Cyanoacetic acid was prepared according to directions in Organic Syntheses (4). It was purified by recrystallization from water and was dried over phosphorus pentoxide. Some difficulty was experienced in the purification of this material and the final product, as shown by analysis for ammonia, was 98% pure. The major impurity is sodium chloride, and, since dilute nitrile solutions were employed, its effect was undoubtedly negligible.

Solutions of nitriles, other than cyanoacetic acid, were prepared by direct weighing. For cyanoacetic acid, solutions of approximately the desired concentration were standardized by complete hydrolysis and determination of ammonia. Reaction mixtures were approximately 0.2 N with respect to nitrile.

Other reagents, procedures, and methods of analysis have been previously described (16).

Results

With the exception of cyanoacetic acid, the consecutive reactions involved in the hydrolysis of the nitriles considered here have been investigated by following the reactions through determination of ammonia, and of total amide and ammonia. The general behaviour is similar to that observed for propionitrile. The relations between rates of nitrile and amide hydrolysis conform to the treatment previously discussed (16). Presentation of these experimental data in detail would therefore seem to be superfluous. The results are summarized in the form of relative rates given in Table I.

Acetonitrile, like propionitrile, provides a system of two irreversible, unimolecular consecutive reactions over the complete range $k_{nitrile} \ll k_{amide}$ (below 4 N acid) to $k_{nitrile} \gg k_{amide}$ (estimated above 11 N acid). This is seen from Table I, where the variations of the rate ratios with acid concentration

TABLE I

RATE RATIOS OF NITRILE AND AMIDE* HYDROLYSIS AT VARIOUS ACID CONCENTRATIONS

System	Hydrochloric acid concentration, normality					
	1.00	4.00	5.02	6.48	8.47	10.13
Propionitrile: propionamide†	1 : 2000	1 : 300	1 : 90	1 : 10	3 : 1	40 : 1
Acetonitrile: acetamide	1 : 2500	1 : 350	1 : 80‡		2 : 1	
Hydrocyanic acid: formamide	1 : 12000	1 : 500§			1 : 3	

* *Reference (15).*

† *Reference (16).*

‡ *k_{amide} obtained by interpolation of neighbouring concentrations.*

§ *$k_{nitrile}$ obtained from Peiker, Ph.D. thesis, McGill University.*

are evidently parallel for propionitrile and acetonitrile. Since the rate of acetonitrile hydrolysis increases markedly in the acid range around 8 *N*, while that of acetamide hydrolysis decreases (6), $k_{acetonitrile}$ will greatly exceed $k_{acetamide}$ at some higher acid concentration, probably above 11 *N* by analogy with propionitrile.

The behaviour of hydrocyanic acid is slightly different. At an acid concentration of 8.47 *N*, the rate of hydrolysis of formamide is faster than that of the nitrile, although it has been almost overtaken. Values of k_{HCN} at this acid concentration, as determined by analysis for ammonia, are less than, but approach, the true value. It is evident that up to concentrations of 7 to 8 *N* the nitrile reaction may be followed by determination of ammonia alone. Since the velocity of hydrolysis of hydrocyanic acid increases so markedly with increase of acid concentration, while that of the amide decreases, such a procedure at acid concentrations above 11 *N* might result in the evaluation of $k_{formamide}$. As the *trends* in rates are clearly evident, it has not appeared necessary to evaluate precise velocity ratios at acid concentrations other than those employed here.

For cyanoacetic acid, the determination of ammonia alone gives satisfactory velocity constants at acid concentrations of 1 and 4 *N*. At 8.47 *N*, however, the familiar, prominent induction period occurs. Evidently, the behaviour of the system, cyanoacetic-acid–malonamic-acid, is similar to that of the other nitriles. Since cyanoacetic is a solid, the analytical technique previously employed for analysis of total amide and ammonia is unsuitable and the reaction velocity has been studied only at acid concentrations of 1 and 4 *N*. Velocity data for malonamic acid hydrolysis are not available, and it is not possible, therefore, to calculate $k_{nitrile}$ at the higher acid concentrations from analytical data on ammonia production.

It is evident that for a sufficient range of acid concentrations, the consecutive reactions for the nitriles studied in the present investigation have characteristics similar to the unique behaviour observed for propionitrile in hydrochloric and sulphuric acids.

The unimolecular velocity constants for a range of temperatures and acid concentrations, as determined by analysis for total ammonia and amide, are recorded in Table II. The constants are the mean, usually, of five to six

TABLE II

UNIMOLECULAR VELOCITY CONSTANTS FOR THE HYDROLYSIS OF HYDROCYANIC ACID, ACETONITRILE, AND CYANOACETIC ACID AT VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID

	Concentration of hydrochloric acid, normality	Concentration of nitrile, normality	Temperature, ° C.	$k \times 10^2$ hr.$^{-1}$
Hydrocyanic acid	1.00	0.4365	65.0	0.180*
			80.3	0.869
			99.9	5.64
	8.47	0.2204	0.0	0.855
			19.8	12.6
			29.7	39.3
			34.7	73.8
Acetonitrile	0.509	0.2011	59.6	0.0132
	1.00	0.2012	59.6	0.0292
			83.5	0.428
			93.3	1.16
			99.7	2.28
			111.8	6.65
	2.00	0.2013	59.6	0.0774
	4.00	0.2014	49.6	0.100
			59.6	0.329
			80.6	3.38
			94.1	13.8
			99.5	22.7
	5.02	0.2315	59.6	0 958
			70.1	3.06
			83.1	10.7
			99.7	49.3
	8.47	0.2217	28.4	2.08
			42.7	9.86
			49.6	20.5
			59.6	54.9
Cyanoacetic acid	1.00	0.1851	99.5	1.01
			110.2	2.67
			125.4	10.2
	4.00	0.1855	59.6	0.225
			90.5	5.65
			99.5	13.5
			109.9	36.5

* *Value obtained from Peiker, Ph.D. thesis, McGill University.*

individual values. The average deviation from the mean was approximately 2 to 3% for cyanoacetic acid and not more than 1 to 2% for the other nitriles. The values at the more dilute concentrations are the more accurate. All concentrations refer to 25° C., and no correction has been applied for variation of collision number with temperature. Errors arising from these approximations will partially cancel and should be negligible for comparative purposes.

The values of A and E calculated from the Arrhenius relations are given in Table III together with values for propionitrile. Values of k/N, expressed in seconds, were employed in the evaluation of A. The error in E is less than 100 to 200 cal. for acetonitrile at 1 and 4 N acid, as determined by comparison of worst and best Arrhenius lines, and less than 300 to 400 cal. for the remaining data. A value of E of 25,300 cal., based on two temperatures only, is recorded for acetonitrile in alcohol–water medium at hydrochloric acid concentration of 0.5 N (5). The hydrolysis of hydrocyanic acid in hydrochloric acid of concentrations up to 7.84 N has been studied over a range of temperatures (7), but neither the rate data nor the precise temperature coefficients are recorded. The statement of Krieble and Peiker (9) that the relative rates of hydrolysis of hydrocyanic acid at different acid concentrations are constant over a temperature range is not in agreement with the present results.

TABLE III

THE ARRHENIUS CONSTANTS FOR THE HYDROLYSIS OF HYDROCYANIC ACID, ACETONITRILE, AND CYANOACETIC ACID AT VARIOUS ACID CONCENTRATIONS

Nitrile	Acid concentration, N	$\log_{10} A$	E, cal.
Hydrocyanic acid	1.00	9.65	24,700
	2.00 4.00	—	24,300*
	8.47	10.65	21,500
Acetonitrile	1.00	10.33	26,500
	4.00	10.30	25,800
	5.02	9.60	24,200
	8.47	9.12	21,100
Cyanoacetic acid	1.00	9.9	26,300
	4.00	9.9	25,500
Propionitrile	1.00	10.04	25,600
	4.00	9.95	24,800
	5.02	9.68	23,900
	6.48	8.92	21,800
	8.47	8.85	20,100
	10.13	8.78	18,900

* *Average value calculated from results of Peiker, Ph.D. thesis, McGill University.*

In general, the magnitude of A found in the present series of studies of nitrile hydrolysis is within a factor of 100 of the so-called "normal" value, on the "slow" side.

Discussion

The nitriles considered in this work have been studied in hydrochloric acid by other investigators (7, 8). They assumed that the velocity of amide hydrolysis is much faster than that of the nitrile over an acid range comparable with that employed here, and they followed the reactions by determination of ammonia. This appears to be satisfactory for hydrocyanic acid since their acid concentration did not exceed 7.84 *N*. However, the results obtained here for acetonitrile, and comparison of their data with those for acetamide (15), show that at a hydrochloric acid concentration of 10 *M* they have essentially measured the hydrolysis of acetamide. Exact comparison of the present results with their data is difficult because of the inaccuracies of interpolation and because the exact amount of amide hydrolysis occurring during their analysis for ammonia is unknown.

On the basis of the present work and the behaviour of propionitrile (13), it is possible to infer something of the nature of the consecutive reactions involved in the hydrolysis of acetonitrile, hydrocyanic acid, and cyanoacetic acid in mineral acids other than hydrochloric. The reactions in sulphuric and hydrobromic acids are of particular interest since these acids have also been employed by others (8, 9) in studies with these nitriles. In sulphuric acid, the rate relation $k_{nitrile} \ll k_{amide}$ should obtain in the more dilute solutions (about 1 to 4 *N*). Since the rate of nitrile hydrolysis in sulphuric acid solutions increases more slowly with acid concentration than in hydrochloric acid solutions (8, 16), the rate of hydrolysis of each nitrile should become comparable with that of the corresponding amide at somewhat higher acid concentrations than for hydrochloric acid. Again, since in sulphuric acid solutions of concentration above 20 *N* the relation $k_{propionitrile} \gg k_{propionamide}$ is found, it might be expected that this rate relation will also be approached for the other nitriles at very high sulphuric acid concentrations. This is supported by the well known fact that amides may be isolated quantitatively from nitriles dissolved in concentrated sulphuric acid.

As with sulphuric acid, the rate of nitrile hydrolysis in hydrobromic acid should become comparable with that of amide hydrolysis at some acid concentration higher than that in hydrochloric acid. However, at the restricted upper limit of hydrobromic acid concentrations ordinarily available (8 *N*), the relation $k_{nitrile} \gg k_{amide}$ would not be attained.

The relative rates of hydrolysis of different nitriles, at given hydrochloric acid concentration, are not governed even in a general way by the differences in activation energy. This may be seen from Fig. 1, where a linear relation of theoretical slope is obviously not obtained. Deviations from the theoretical relation may be attributed to variations in the *A* factor, which result from the proximity of the substituent to the seat of reaction and are characteristic of the effect of structural change in most reactions of aliphatic compounds (18). Simultaneous variations of *A* and *E* make analysis of the relation between rate

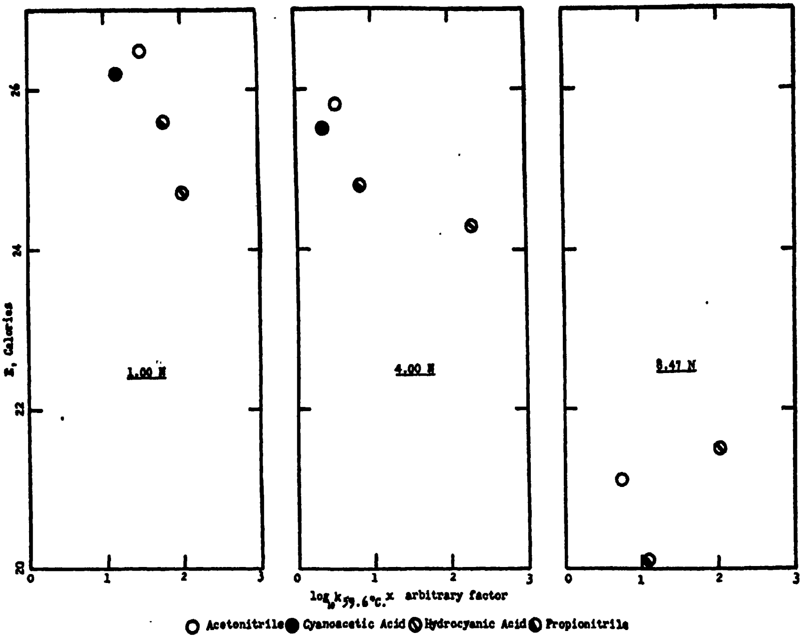


FIG. 1. *Plot of* $\log_{10} k_{59\cdot 6°C.}$ *against E for different nitriles, at three acid concentrations.*

and structure difficult (2, pp. 120, 123). This is immediately apparent from the fact that the rate of propionitrile hydrolysis is intermediate between that of hydrocyanic acid and that of acetonitrile. It has been suggested (8) that the rate of nitrile hydrolysis increases with the basylous nature of the group on the cyano function. In this respect, an investigation of meta and para substituted benzonitriles, for which the A factor would probably be constant (2, pp. 120, 123), would be of interest.

The rapid increase in rate of nitrile hydrolysis with acid concentration has been interpreted in several ways. Results on the hydrolysis of cyanamide in nitric acid solutions of concentration up to 5 N have been expressed by a relation analogous to that for the primary exponential salt effect (1), and have also been related to the acidity function, H_0, of Hammett (3). Molecular catalysis has also been postulated (9), and, for hydrocyanic acid, a linear relation was obtained between log k and the logarithm of the activity of undissociated hydrochloric acid molecules.

The hydrolysis of acetonitrile in hydrochloric acid of concentrations up to 4 to 5 N displays accordance with all these relations. This may be seen from

Fig. 2, where rate is plotted against normality, H_0, and log $a^2_\pm$. The slope of the log k vs. H_0 line is 0.92. At higher concentrations where the variation in E is also most marked, deviations from these relations appear. There is at present no theoretical basis for the interrelation of primary salt effect, acidity function, and log $a^2_\pm$, and some of these relations are probably fortuitous. It would appear, moreover, that the fundamental character of all the relations found here is open to doubt, in view of the simultaneous variations of the Arrhenius constants (Table III). Such variations, as discussed in an earlier paper (16), appear to be real. The plot of log k/N against E, for acetonitrile, is a line, the slope of which is of proper order, although shifted in the direction indicated by the simultaneous variation in A (Fig. 2). This behaviour is similar to that observed with propionitrile where the rate increase also followed the decrease in activation energy.

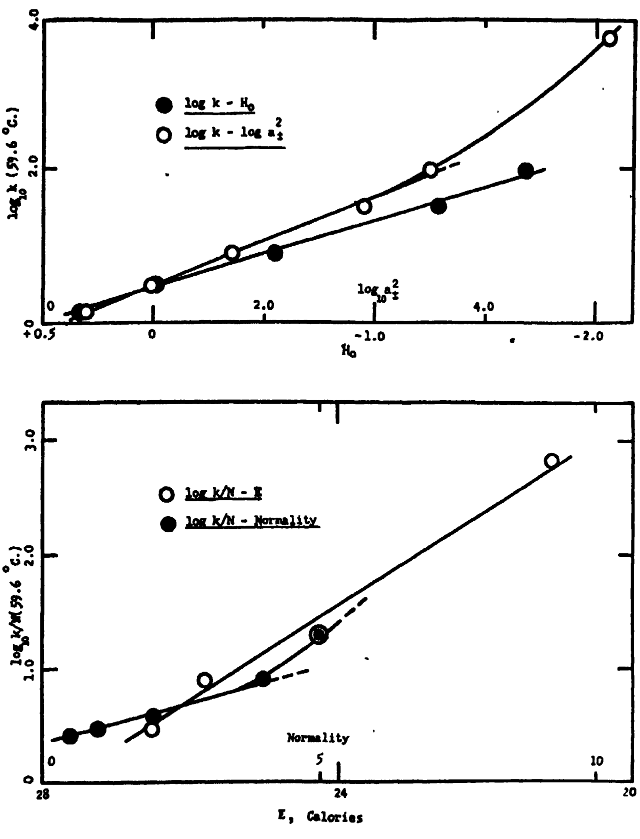


FIG. 2. *Plots of some rate relations.*

With hydrocyanic acid, the rate increase with acid concentration is faster than that for the other nitriles. The decrease in E is smaller than that for acetonitrile or propionitrile, but a simultaneous increase in the *A* term occurs. This opposing variation of *A* and *E* is contrary to the behaviour generally found but accounts in this case for the observed behaviour. The Hammett relation does not hold for hydrocyanic acid. In view of the observed changes with acid concentration in *E* and *A* for hydrocyanic acid hydrolysis, remarks similar to those made for acetonitrile apply to the relation between rate and square of the mean ion activity, noted particularly for this nitrile.

Explanation of the variation of activation energy with acid concentration observed in the nitrile and amide hydrolysis reactions encounters difficulties. These arise not only from the complexity of highly concentrated solutions of electrolytes, but also because bimolecular reactions involving complex organic molecules, particularly where the solvent participates in the reaction, are most difficult of treatment (14). The dependence of the activation energy of ionic reactions on dielectric constant, ionic strength, and composition of the solution has been pointed out (17). Although of lesser importance for reactions involving neutral molecules, these aspects should be considered. This is very difficult in studies of the variation of rate with acid concentration in concentrated acid media, as simultaneous variations in composition and dielectric constant occur and information concerning the variation of dielectric constant with composition is not obtainable.

The variation of activation energy found in the present studies of nitriles is in the same direction as that found by Leininger and Kilpatrick for the hydrolysis of sucrose (10) and ethylal (11) in concentrated hydrochloric acid. They have explained this variation in terms of a variation of the heat content of the activated intermediate with acid concentration, which is determined principally by the heat of dilution of the oxonium ion, H_3O^+. In this way, it is possible to account for an activation energy decrease with increase in acid concentration. This explanation appears analogous to an earlier conclusion (14) that the Arrhenius parameters depend on the internal volume change for the reaction and particularly on the relative solvation of reactants and complex, which presumably depends on concentration.

The change in *E* with acid concentration is specific for a variety of substrates and a given acid catalyst, or for a variety of catalysts and a given substrate. This would denote in each instance a variable influence on the activation energy of the heats of dilution of substrate and complex.

It appears that there may be a relation between the acidity function, H_0, and the variation of activation energy with acid concentration exhibited by some acid catalyzed reactions. Of the three reactions cited by Hammett and Paul (3), the rates of which demonstrate the H_0 relation, hydrolysis of sucrose, cyanamide, and ethyl acetate, the hydrolysis of sucrose shows dependence of *E* on concentration. Also, since the hydrolysis of nitriles exhibits both Hammett's relation and dependence of *E* on concentration, the hydrolysis of cyanamide may well display the same behaviour. The activation energy for the acid hydrolysis of ethyl acetate in highly concentrated solutions does not appear to have been examined. However, data reported for hydrochloric acid solutions below 0.4 N (19) give an indication that in concentrated solutions there may be an activation energy decrease with increasing acid concentration.

A parallelism between the H_0 relation and E change may be explained by variation of solvation of the oxonium ion with change of acid concentration. As previously mentioned, decrease of solvation could account for the decrease of activation energy with increasing acid concentration. At the same time, removal of an envelope of water molecules from the oxonium ion would increase the proton transfer tendency, of which H_0 is a measure.

References

1. GRUBE, G. and SCHMID, G. Z. physik. Chem. 119 : 29-45. 1926.
2. HAMMETT, L. P. Physical organic chemistry. McGraw-Hill Book Company, Inc., New York and London. 1940.
3. HAMMETT, L. P. and PAUL, M. A. J. Am. Chem. Soc. 56 (4) : 830-832. 1934.
4. INGLIS, J. K. H. Org. Syntheses, Collective Vol. I : 249-251. 1932.
5. KILPI, S. Z. physik. Chem. 86 : 641-681. 1914.
6. KRIEBLE, V. K. and HOLST, K. A. J. Am. Chem. Soc. 60 (12) : 2976-2980. 1938.
7. KRIEBLE, V. K. and MCNALLY, J. G. J. Am. Chem. Soc. 51 (11) : 3368-3375. 1929.
8. KRIEBLE, V. K. and NOLL, C. I. J. Am. Chem. Soc. 61 (3) : 560-563. 1939.
9. KRIEBLE, V. K. and PEIKER, A. L. J. Am. Chem. Soc. 55 (6) : 2326-2331. 1933.
10. LEININGER, P. M. and KILPATRICK, M. J. Am. Chem. Soc. 60 (12) : 2891-2899. 1938.
11. LEININGER, P. M. and KILPATRICK, M. J. Am. Chem. Soc. 61 (9) : 2510-2514. 1939.
12. LEWCOCK, W. Pharm. J. 101 : 50-51. 1918.
13. MCLEAN, J. D., RABINOVITCH, B. S., and WINKLER, C. A. Can. J. Research, B, 20 (8) : 168-173. 1942.
14. OGG, R. A., JR. and RICE, O. K. J. Chem. Phys. 5 : 140-143. 1937.
15. RABINOVITCH, B. S. and WINKLER, C. A. Can. J. Research, B, 20 (5) : 73-81. 1942.
16. RABINOVITCH, B. S., WINKLER, C. A., and STEWART, A. R. P. Can. J. Research, B, 20 (7) : 121-132. 1942.
17. WARNER, J. C. Ann. New York Acad. Sci. 39 (5) : 345-354. 1940.
18. WATSON, H. B. Ann. Rept. Chem. Soc. (London) 35 : 236-251. 1938.
19. WYCZALKOWSKA, W. Roczniki Chem. 14 : 1118-1122. 1934.
20. ZIEGLER, K. Org. Syntheses, Collective Vol. I : 307-309. 1932.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. NOVEMBER, 1942 NUMBER 11

AROMATICS IN TURNER VALLEY CRUDES[1]

BY L. HENDRICKSON[2], A. T. HUTCHEON[3], AND J. W. T. SPINKS[4]

Abstract

A dispersion method has been developed for the determination of aromatics in the presence of paraffinic and naphthenic hydrocarbons. The method has been applied to selected cuts obtained by fractionation of Turner Valley crudes. The percentages of benzene, toluene, and the xylenes occurring in a series of Turner Valley crudes have been determined.

Introduction

The determination of aromatic compounds in a mixture of hydrocarbons is of considerable importance in a number of problems. The methods commonly employed involve either direct estimation by means of a chemical reaction such as sulphonation or nitration (3, 8), or estimation by means of some physical property such as density (5, 17), aniline point (18), refractivity (2, 7, 10, 11, p. 1737, 13, 14, 20), or dispersion.

In the following paragraphs the dispersion method for the determination of benzene, toluene, and the xylenes is described. The results of the application of the method to certain Turner Valley crude oils are presented.

Specific Dispersion Method

The refractive index of a substance usually varies with wave-length. The dispersion, Δ_{X-Y}, is equal to the difference between the refractive indices for light of wave-lengths X and Y. $\Delta_{X-Y} = n_X - n_Y$. Similarly, the specific dispersion, δ'_{X-Y} equals $r_X - r_Y$, where r is the specific refractivity. Using the Gladstone–Dale expression for specific refractivity,

$$\delta'_{X-Y} = \frac{n_X - 1}{d} - \frac{n_Y - 1}{d} = \frac{n_X - n_Y}{d},$$

where d = density. The number so obtained is commonly multiplied by 10^4, so that

$$\delta_{X-Y} = (\delta'_{X-Y})10^4 = \left(\frac{n_X - n_Y}{d}\right)10^4.$$

δ_{X-Y} is loosely spoken of as the specific dispersion. The Lorentz–Lorenz formula for specific refractivity, $\frac{n_x^2 - 1}{n_x^2 + 2} \cdot \frac{1}{d}$, may be used, but in most of the work described in the literature, the simpler Gladstone–Dale expression is employed. The densities are usually determined at 20° C. and referred to water at 4° C., i.e., d_4^{20}. The refractive indices are commonly determined at 20° C. for one or other of two pairs of lines, either the *F* and *C* hydrogen lines (4861 and 6563 Å), or the *g* and *e* mercury lines (4358 and 5461 Å respectively). The specific dispersions so obtained (multiplied by 10^4) are δ_{F-C}^{20} and δ_{g-e}^{20}, respectively, e.g., $\delta_{g-e}^{20} = \frac{n_g^{20} - n_e^{20}}{d_4^{20}} \cdot 10^4$.

---

[1] *Manuscript received in original form June 15, 1942, and as revised, August 21, 1942. Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*

[2] *Fourth year student; at present with Hudson Bay Mining and Smelting Company, Flin Flon, Man.*

[3] *Graduate assistant; at present with Shawinigan Chemicals Ltd., Shawinigan Falls, Que.*

[4] *Professor of Physical Chemistry.*

Dispersivity is pre-eminently a constitutive property and is said to be much more sensitive to structural differences than refractivity (1, 4). Ward and Kurtz (20) have collected and classified a great mass of data on the properties of hydrocarbons and have plotted δ_{F-C}^{20} against boiling point for each of the main classes of hydrocarbons. On inspection of their curves, some striking regularities are apparent: (*a*) the paraffins and naphthenes have a constant specific dispersion of 99, irrespective of boiling point; (*b*) the cyclic mono-olefines have a constant specific dispersion of 118; (*c*) the value for non-cyclic mono-olefines approaches that for the cyclic mono-olefines as the boiling point increases; (*d*) for the aromatics, specific dispersion is much higher than for the paraffins and naphthenes, and decreases with substitution in the benzene ring.

The method for determining aromatics in hydrocarbon mixtures by dispersion measurements is based on conclusions which may be drawn from these curves. For instance, it is apparent that if a crude that is free from olefines is fractionated so that each cut contains only one of the aromatics, the fraction may be treated as a mixture of two components. One component will be the aromatic and the other will be a mixture of the naphthenes and paraffins. The mixture of naphthenes and paraffins may be treated as a single component since members of these two hydrocarbon classes have nearly the same specific dispersion, irrespective of molecular weight or boiling point.

MacFarlane and Wright (16) have found that refractivity follows the mixture rule very closely when compositions are calculated on a volume basis. Small deviations are observed when compositions are calculated on a weight or mole basis. Specific dispersion also follows the mixture rule.

The first serious attempt to utilize specific dispersions for hydrocarbon analysis was made by Darmois in 1920 (6). Since then, Ward and Fulweiler (19), Fuchs and Anderson (10), Ward and Kurtz (20), and Grosse and Wackher (12) have furthered the development and enlarged the field of utility of the method. The present method follows that of Grosse and Wackher rather closely but differs in that the mercury lamp, instead of a hydrogen tube, is used as light source.

Experimental

Measurement of Dispersion

The Pulfrich refractometer with temperature control was used to determine the dispersion at 20° C. for the *e* and *g* lines from a mercury vapour lamp. The *e* and *g* lines from an ordinary mercury vapour lamp are usually much more intense than the *F* and *C* lines from a hydrogen tube, and this is a factor of some importance when many dispersions have to be measured. The dispersion can be measured rapidly and the resulting specific dispersion should have an accuracy of 0.1 to 0.2 units.

Alternatively, the Abbé refractometer may be used to determine dispersions but the accuracy obtainable is only about one-tenth that obtainable with a Pulfrich refractometer. Fuchs and Anderson (10) describe a dispersometer that is said to be more easily manipulated than the Pulfrich and achieves an accuracy of one dispersion unit.

Measurement of Density

The relative density, d_{20}^{20}, can be measured with a sufficient degree of accuracy using a Mohr–Westphal balance (9). Where only small quantities of liquid are available a pycnometer may be used.

Verification of Method

Known series were made up, on a weight percentage basis, in which an aromatic was mixed with a paraffin of approximately the same boiling point range. The series were made up of

(*a*) Mixtures of benzene and hexane,

(*b*) Mixtures of toluene and 2,2,4-trimethyl pentane,

(*c*) Mixtures of 2,2,4-trimethyl pentane with a mixture of the isomeric xylenes.

Data for the series are recorded graphically in Fig. 1. Data concerning the materials are given in Table I. It is seen that, in agreement with the results of other workers, the weight percentage composition is a linear function of the specific dispersion. With care and some practice, compositions can be determined to ±1% using specific dispersions.

TABLE I

MATERIALS

Material	Maker	Grade	d_4^{20}		n_D^{20}	
			Actual	Literature	Actual	Literature
Benzene	Merck	Reagent	0.8779	0.8789	1.50067	1.50165
Toluene	Merck	Purified	.8643	.8669	1.49578	1.49552
Xylene	Merck	Reagent	.8656		1.49775	
Hexane	Eastman	Pract.	.6621	.6595	1.37567	1.37515
2,2,4-Trimethyl pentane	Eastman	Tech.	.6947	.6918	1.39331	1.39162

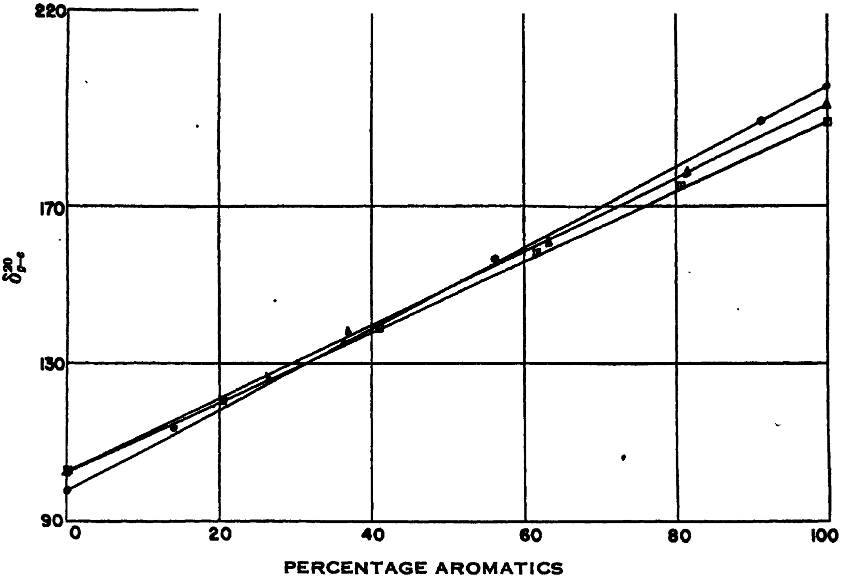


FIG. 1. *δ^{20}_{g-e} vs. percentage aromatics:* ⊙, *benzene and hexane;* △, *toluene and 2,2,4-trimethyl pentane;* ⊡, *xylene and 2,2,4-trimethyl pentane.*

Application to Turner Valley Crudes

Previous work (7, 21) has shown that when Turner Valley crudes are fractionated in Stedman columns, the cut from 60 to 90° C. will contain all the benzene, the cut from 90 to 120° C. all the toluene, and the cut from 120 to 150° C. all the xylenes. The crudes do not contain unsaturates and thus no allowance need be made for them (unsaturates can be allowed for by determination of the bromine number (12)).

The dispersions of the hydrocarbons vary slightly with boiling point and it is therefore necessary, in accurate work, to determine so-called base values for the different cuts. The base value is the specific dispersion for the hydrocarbons, other than aromatics, present in the cut. For example, the xylene cut from crude oil from Foundation 1 well, after removal of aromatics by nitration, gave the following data: $d_4^{20} = 0.7236$, $n_g^{20} = 1.41209$, $n_e^{20} = 1.40480$, whence $\delta^{20}_{g-e} = 100.7$

As a result of numerous determinations, the following base values are suggested: for the benzene cut, 97.3; for the toluene cut, 99.1; for the xylene cut, 100.5. The specific dispersions, δ^{20}_{g-e} for benzene, toluene, and xylene were found to be 201.2, 196.3, and 192.0 respectively (for details of measurements see thesis by L. Hendrickson, University of Saskatchewan, 1941). Using these values and the appropriate base value, the following formulae are easily derived (based on a linear relation between specific dispersion and weight per cent composition, W):

Benzene cut: $\delta^{20}_{g-e} = 97.3 + 1.039\ W.$
Toluene cut: $\delta^{20}_{g-e} = 99.1 + 0.972\ W.$
Xylene cut: $\delta^{20}_{g-e} = 100.5 + 0.915\ W.$

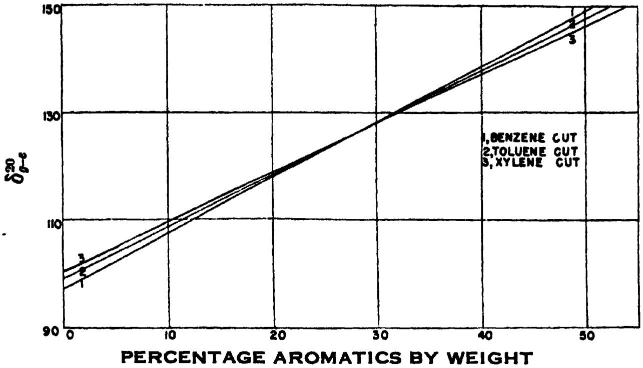


FIG. 2. δ^{20}_{g-e} *vs. percentage aromatics for cuts from Turner Valley crudes.*

These relations are represented graphically in Fig. 2. It should be remembered that this figure applies to cuts from Turner Valley crudes from the paleozoic limestones and to dispersions determined for the *g* and *e* mercury lines.

The curves have been checked by measurements of dispersion on samples made up by weight; for example, from reagent toluene plus the toluene cut freed from aromatics by nitration. They have also been checked by determinations of aromatics in numerous samples by nitration as well as by dispersion (see, for example, Table IV).

Formulae giving the percentages of aromatics are:

60 to 90° C. cut: wt. % benzene $= 0.962\ \delta^{20}_{g-e} - 93.6$
90 to 120° C. cut: wt. % toluene $= 1.029\ \delta^{20}_{g-e} - 102.0$
120 to 150° C. cut: wt. % xylenes $= 1.093\ \delta^{20}_{g-e} - 109.8$

The value for the xylenes will be approximate only since a mixture, containing 92% *m*-xylene, was used in determining the curve for xylene, and there is no assurance that the isomers will be present in the same proportions in the cut as in the calibrating mixture. However, the error should not be serious since the specific dispersions of *o*-, *m*-, and *p*-xylene lie within 1% of one another (see, for example (12)).

Procedure

A 1000 cc. sample of crude oil was fractionated in a 3 ft. Stedman column (21) 1 in. in diameter. The ratio of reflux to product was 15 : 1. Cuts were made at 60 to 90°, 90 to 120°, and 120 to 150° C. Determinations of the density and dispersion of each cut were carried out; from these the specific dispersion could be calculated and the percentage aromatics determined.

TABLE II

FRACTIONATION IN A 3 FT. STEDMAN COLUMN, 1 IN. IN DIAMETER

Charge: 1000 cc. at 24° C. Barometer, 720 mm. Ratio reflux: product = 15 : 1

Sample No.	Temperature range, °C, (corr.)	Volume per cent distilled						
		Royalite 45	Foothills 6	N.W. Hud. Bay 2	Foundation 1	Home-Millarville	Royalite 31	Royalite 43
1	I.B.P.—60	2.0	3.2	1.05	6.15	2.57	2.50	1.65
2	60 - 90	5.6	5.3	4.0	9.64	5.25	5.49	7.06
3	90 - 120	9.1	8.3	7.85	13.34	7.80	8.40	7.86
4	120 - 150	7.6	7.1	8.6	10.3	6.47	7.66	6.20
Residue		66.4	69.5	72.1	51.5	70.0	69.8	70.0
Loss		9.3	6.6	6.4	9.1	7.91	6.15	7.23

TABLE III*a*

DISPERSION DATA ON CUTS

Sample No.	Royalite 45			Foothills 6		
	2	3	4	2	3	4
n_g^{20}	1.40664	1.42791	1.44633	1.40543	1.42864	1.44824
n_e^{20}	1.39902	1.41917	1.43045	1.39777	1.41987	1.43824
$n_g^{20} - n_e^{20}$	0.00762	0.00874	0.00988	0.00766	0.00877	0.0100
d_4^{20}	0.7069	0.7442	0.7725	0.7036	0.7477	0.7728
δ_{g-e}^{20}	107.8	117.5	128	108.9	117.2	129.3
Per cent aromatics in cut	9.7	18.5	30.0	10.8	18.5	31.5

TABLE III*b*

DISPERSION DATA ON CUTS

Sample No.	N.W. Hudson's Bay 2			Foundation 1	
	2	3	4	2	3
n_g^{20}	1.40802	1.42990	1.44536	1.40391	1.42616
n_e^{20}	1.40036	1.42103	1.43563	1.39643	1.41760
$n_g^{20} - n_e^{20}$	0.00766	0.00885	0.00973	0.00748	0.00856
d_4^{20}	0.7119	0.7505	0.7728	0.7038	0.7433
δ_{g-e}^{20}	107.6	117.9	126	106.3	115.2
Per cent aromatics in cut	9.7	19.0	27.8	7.0	16.5

TABLE III*c*

Dispersion data on cuts

Sample No.	Royalite 31			Royalite 43		
	2	3	4	2	3	4
n_g^{20}	1.40765	1.43015	1.44743	1.40590	1.43207	1.44918
n_e^{20}	1.40014	1.42137	1.43776	1.39854	1.42316	1.43934
$n_g^{20} - n_e^{20}$	0.00751	0.00878	0.00967	0.00736	0.00891	0.00984
d_4^{20}	0.7100	0.7468	0.7720	0.7037	0.7483	0.7733
δ_{g-e}^{20}	105.8	117.6	125.2	104.5	119.1	127.3
Per cent aromatics in cut	8.1	18.85	26.7	6.9	20.5	29.1

TABLE III*d*

Dispersion data on cuts

Sample No.	Home Millarville 2			
	2	3A*	3B*	4
n_g^{20}	1.40802	1.42384	1.44333	1.44508
n_e^{20}	1.40045	1.41556	1.43333	1.43528
$n_g^{20} - n_e^{20}$	0.00757	0.00828	0.01000	0.00980
d_4^{20}	0.7107	0.7381	0.7657	0.7688
δ_{g-e}^{20}	106.7	112.1	130.6	127.5
Per cent aromatics in cut	9.0	13.3	32.2	29.5

* *Cut 3 in two parts: 3A, 88 to 103° C., 5%*
3B, 103 to 119° C., 2.8% } *7.8% (See Table II)*

The percentage aromatics in a large number of samples was checked by nitration (3). The agreement obtained was good and is illustrated by a few results obtained on the toluene cuts (see Table IV). The nitrations were

TABLE IV

Percent toluene (by wt.) in cut

—	Home-Millarville 2	Royalite 31	Royalite 43
Dispersion	13.3	18.8	20.5
Nitration	12.9	18.84	20.26

run in duplicate. The percentage aromatics in a given cut being known, that in the crude can be calculated.

Example. Foundation 1: Percentage toluene in cut 3 = 16.5. Density of cut = 0.7433. Volume of cut expressed as percentage of crude = 13.34. Density of crude oil = 0.7936. Percentage toluene by wt. in crude $= \dfrac{13.34 \times 16.5 \times 0.7433 \times 10}{793.6} = 2.05.$

The results are summarized in Table V, which shows the location and depth of the well, together with the A. P. I. gravity of the crude.

TABLE V

ESTIMATE OF AROMATICS IN TURNER VALLEY CRUDES

Well	Location	Depth, ft.	A.P.I. at 60° F.	Per cent by wt. in crude oil		
				Benzene	Toluene	Xylenes + ethyl benzene
North Turner Valley						
Home-M. 2	6 of 33, 20-3, *W*-5	8495	40.4	0.41	1.44	1.79
Foothills 6	5 of 27, 20-3, *W*-5	8140	41.9	0.49	1.34	2.1
Royalite 43	2 of 22, 20-3, *W*-5	8800	41.1	0.42	1.48	1.71
Central Turner Valley						
Royalite 45	14 of 5, 19-2, *W*-5	7486	44.1	0.48	1.52	2.2
South Turner Valley						
Sterl. Pac. 3*	14 of 33, 18-2, *W*-5	6788	45.8	0.35	2.18	2.71
Royalite 31	6 of 29, 18-2, *W*-5	8064	39.4	0.38	1.44	1.92
Foundation 1	5 of 21, 18-2, *W*-5	6474	46.8	0.63	2.05	
N.W.H. Bay 2	9 of 8, 18-2, *W*-5	7591	39.0	0.33	1.30	2.2

* *Taken from Donald (7).*

The wells investigated give a reasonable cross-section of the Turney Valley field, and, as far as can be seen, there is no relation between aromatic content and position in the field. However, it can be stated in a general way that the lighter the crude, the greater the percentage of toluene. A comparison with crudes from other fields is difficult. As is well known, certain Borneo crudes are very high in aromatics but North American oils are usually relatively poor in aromatics, e.g., one well in the Oklahoma field contains 0.3% toluene (15).

Acknowledgments

Thanks are here extended to the National Research Council of Canada for a grant to one of the writers (Alan T. Hutcheon) and to the Imperial Oil of Calgary for samples of crude oil.

References

1. Allsopp, C. B. and Willis, H. F. Proc. Roy. Soc. (London) A, 153 : 379-391, 392-406. 1935.
2. Brühl, J. W. J. Chem. Soc. 91 : 115-122. 1907.
3. Bruun, J. H. and Hicks-Bruun, M. M. J. Research Natl. Bur. Standards 6(5) : 869-879. 1931.
4. Cohen, J. B. Organic chemistry for advanced students. Vol. 2. 5th ed. Edward Arnold & Co., London. 1928.
5. Colman, H. G. and Yeoman, E. W. J. Soc. Chem. Ind. 38 : 82T-83T. 1919.
6. Darmois, E. Compt. rend. 171 : 952-955. 1920; 172 : 1102-1105. 1921.
7. Donald, R. M. Can. J. Research, B, 18(1) : 12-29. 1940.
8. Faragher, W. F., Morrell, J. C., and Levine, I. M. Ind. Eng. Chem. Anal. Ed. 2(1) : 18-24. 1930.
9. Findlay, A. Practical physical chemistry. 6th ed. rev. and enl. Longmans, Green, and Company, London. 1935.
10. Fuchs, G. H. and Anderson, A. P. Ind. Eng. Chem. 29(3) : 319-325. 1937.
11. Gilman, H. Organic chemistry. Vol. 2. J. Wiley & Sons, Inc., New York. 1938.
12. Grosse, A. V. and Wackher, R. C. Ind. Eng. Chem. Anal. Ed. 11(11) : 614-624. 1939.
13. Kurtz, S. S., Jr. and Headington, C. E. Ind. Eng. Chem. Anal. Ed. 9 : 21-25. 1937.
14. Kurtz, S. S., Jr. and Ward, A. L. J. Franklin Inst. 222(5) : 563-592. 1936.
15. Leslie, R. T. and White, J. D. J. Research Natl. Bur. Standards, 15(3) : 211-225. 1935.
16. MacFarlane, W. and Wright, R. J. Chem. Soc. 114-118. 1933.
17. Thole, F. B. J. Soc. Chem. Ind. 38 : 39T-43T. 1919.
18. Tizard, H. T. and Marshall, A. G. J. Soc. Chem. Ind. 40 : 20T-25T. 1921.
19. Ward, A. L. and Fulweiler, W. H. Ind. Eng. Chem. Anal. Ed. 6(6) : 396-400. 1934.
20. Ward, A. L. and Kurtz, S. S., Jr. Ind. Eng. Chem. Anal. Ed. 10(10) : 559-576. 1938.
21. Watson, L. M. and Spinks, J. W. T. Can. J. Research, B, 18(12) : 388-404. 1940.

STUDIES IN URETHANES

VII. REACTIONS OF ACYL DIURETHANES WITH AMMONIA AND PRIMARY AMINES. STABILIZING EFFECT OF THE PHENYL RADICAL IN PHENYLMALONYL- AND PHENYLSUCCINYL-DIURETHANE[1]

By S. Basterfield[2] and A. J. Dyck[3]

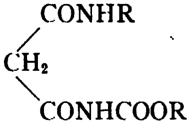
Abstract

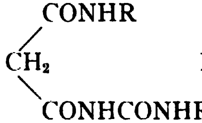
In previous studies it has been shown that the mechanism of decomposition of acyl diurethanes by ammonia and amines is correlated to some extent with the strength of the acid from which the acyl radical is derived and of the base used as ammonolytic reagent. In the oxalic acid series a diurea was obtained from succinyl-diurethane and aniline, but not from oxalyl- or malonyl-diurethane. Succinyl-diurethane gave no diurea with stronger bases.

It is shown in the present study that phenylmalonyl-diurethane yields with aniline a diurea which undergoes rapid decomposition on being heated with aniline at 150° C. Phenylsuccinyl-diurethane gives with aniline a diurea that is much more stable than the one obtained from succinyl-diurethane, as judged by the rate of decomposition on heating with aniline at 150°. No definite evidence of diurea formation was obtained with bases stronger than aniline.

In previous studies on the reactions of acyl diurethanes with ammonia and amines (2, 3), it has been shown that:

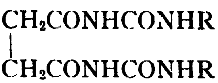
(*a*) Oxalyl-, malonyl-, and phthalyl-diurethanes are decomposed with the loss of one or both urethane (carbethoxy-amino) groups and the formation of amides of the dibasic acids, or of urethano- and ureido-amides (I, II)


I


II

without the appearance of acyl diureas;

(*b*) Succinyl-, glutaryl-, and adipyl-diurethanes yield, with ammonia and ethylamine, amides, but with aniline, acyl diphenylureas (III)


III

$$\begin{array}{l} CH_2CONHCONHR \\ | \\ CH_2CONHCONHR \end{array} \qquad III$$

which are decomposed by further action of the base into anilides of the dibasic acids and diphenylurea. It was pointed out that the tendency of diurethanes to lose urethane groups and give amides rather than diureas is correlated in some measure with the strength of the acid from which the acyl radical is derived and that of the base used as ammonolytic reagent.

---

[1] *Manuscript received in original form June 27, 1942, and as revised, August 31, 1942. Contribution from the Chemical Laboratory, University of Saskatchewan, Saskatoon, Sask.*

[2] *Dean of Regina College, formerly Professor of Organic Chemistry, University of Saskatchewan.*

[3] *Sometime Advisory Soil Chemist, Rubber Institute, Kuala Lumpur, Malaya. Formerly graduate student, University of Saskatchewan and MacDonald College, Quebec.*

As a further contribution to this problem an examination has been made of the effect on the course of the reactions of introducing a phenyl radical into the acyl groups of malonyl- and succinyl-diurethane. The influence of the phenyl radical on the ionization constants of malonic and succinic acids is shown in Table I. The value in both instances is considerably more than doubled. Since malonyl-diurethane with aniline gave no evidence of diurea formation while succinyl-diurethane yielded a diurea, it might be expected, considering the factor of acid strength alone, that phenylmalonyl-diurethane would not yield a diurea while phenylsuccinyl-diurethane might or might not do so, seeing that the ionization constant of phenylsuccinic acid lies between that of malonic acid and that of succinic acid in the region 10^{-4}.

TABLE I

TABLE OF IONIZATION CONSTANTS

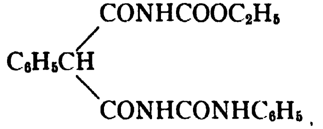
Acid	K
Malonic	1.23×10^{-3}
Phenylmalonic	2.77×10^{-3} (1)
Succinic	6.6×10^{-5}
Phenylsuccinic	1.58×10^{-4}

The presence of a phenyl radical, however, intrudes another factor into the situation. The stabilizing effect of the phenyl radical on relatively unstable molecules has long been recognized, and has been attributed in recent physicochemical theory to the resonant property of the benzene ring. This effect would tend to offset the influence of the first factor, and the formation and persistence of a diurea might well depend on which influence was dominant. Furthermore if a diurea were formed from phenylsuccinyl-diurethane its stability might readily be compared with that of succinyldi-(phenylurea).

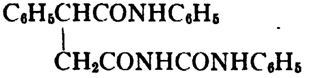
Experiment showed that the stabilizing influence of the phenyl radical was operative, since both phenylmalonyl- and phenylsuccinyl-diurethane gave diureas during two hours' heating with aniline, the first at 15C° C. and the second at 180° C. Phenylsuccinyldi-(phenylurea) is unquestionably more stable than succinyldi-(phenylurea), as shown by its rate of decomposition with aniline. The succinyl compound was obtained after one hour's heating of the diurethane with aniline, and it disappeared entirely during a second hour's heating at the same temperature. The phenylsuccinyl compound was obtained in good yield after two hours' heating of the diurethane at 180°, and the diurea was still present in considerable amount after a third hour of heating at 180° to 200°. Even allowing for a difference in the rates of formation of the diureas, it seems safe to conclude that the phenylsuccinyl-diurea is the more stable.

Phenylmalonyldi-(phenylurea) has a stability much closer to that of succinyldi-(phenylurea), though it is difficult to make an accurate comparison. The succinyl compound was formed and decomposed during two hours' heating at 150° C., while the phenylmalonyl compound was isolated after two hours' heating, together with phenylmalonanilide (28%) and diphenylurea, indicating that some decomposition of the diurea had taken place. It is true that each diurea was completely decomposed during one hour's heating at 150°, and this suggests about equal stability for the two compounds. The fact, however, that in the original preparation of the phenylmalonyl compound there was undecomposed diurea still present after two hours' heating suggests that perhaps it is somewhat more stable than succinyldi-(phenylurea). This would be more certain if the rates of formation of the two diureas were of the same order, a not unreasonable assumption, though no data on this point have been obtained.

From the reaction of phenylmalonyl-diurethane with aniline at 150° C. a small quantity of another product was obtained. Its identity was not established satisfactorily by analysis, but because of its relatively low melting point, 151° C.*, it was regarded as impure phenylureido-phenylmalonyl-urethane (IV) analogous to the phenylureido-succinylurethane, m.p. 163°,


IV

obtained in an earlier study (2), rather than phenylureido-phenylmalon-anilide. Such a ureido-anilide was obtained, however, from phenylsuccinyl-diurethane (V)†. It melted at 234° and was isolated from the reaction mixture after three hours' heating at 180° to 200°.


$$\begin{array}{l} C_6H_5CHCONHC_6H_5 \\ | \\ CH_2CONHCONHC_6H_5 \end{array} \qquad V$$

It probably represents a stage in the decomposition of the acyldi-(phenyl-urea) to the acyldi-anilide.

It should be noted that considerable difficulty was experienced in obtaining some of the products of the above reactions reasonably pure. The diureas, anilides, and intermediate products often required tedious recrystallization to free them from related compounds. The melting points of the diureas, of phenylureido-phenylsuccinanilide and of diphenylurea all lie within the range 234° to 237°.‡ Since diphenylurea was a constant product of prolonged reaction with aniline it was necessary to establish its identity repeatedly by a mixed melting point determination with a known sample.

One experiment was made on the decomposition of malonyl-diurethane with aqueous cyclohexylamine (30%). A good deal of gummy material was obtained but from it were isolated malon-dicyclohexyl-amide and urethane. This base thus resembled ethylamine in its action.

---

* *All melting points are uncorrected.*

† *Cf. also malonyl-diurethane (3).*

‡ *Cf. phenylureido-malonanilide (3).*

Experimental

Preparation of Acyl Diurethanes

Phenylmalonyl-diurethane, $C_6H_5CH\,.\,(CONHCOOC_2H_5)_2$. This compound was prepared, as described in a previous paper (2), from phenylmalonic acid, phosphorus oxychloride, and urethane; m.p., 154° C. Yield, about 25%.

Phenylsuccinyl-diurethane, $C_6H_5CH\,.\,CH_2(CONHCOOC_2H_5)_2$. Phenylsuccinic acid, urethane, and phosphorus oxychloride in suitable proportions were mixed together and allowed to stand at room temperature for several days. The temperature was then raised to 40° C. for six hours, and finally to 50° for two to three hours. The semisolid mass was left in contact with water overnight, and the white solid obtained recrystallized from alcohol; m.p., 162° C. Yield, about 15%. Calc. for $C_{16}H_{18}N_2O_6$: N, 8.38%. Found: N, 8.42, 8.47%. In this preparation, considerable blackening of the reaction mixture occurs if the temperature is raised only moderately immediately after the reactants are mixed. The procedure outlined above gave the best results although the yield was disappointing.

Reactions of Phenylmalonyl-diurethane

With ammonia. Three grams of the diurethane was mixed with 25% aqueous ammonia and allowed to stand for a week at room temperature. A white precipitate formed. It was identified as phenylmalonamide, previously prepared by Dox and Yoder (4); m.p., 232° C. Calc. for $C_9H_{10}N_2O_2$: N, 15.73%. Found: N, 15.50, 15.50%. The ammoniacal filtrate was evaporated at 50° and the residue extracted with ether. The ether extract yielded urethane. The ether insoluble residue (0.2 gm.) decomposed at 270° to 280°. It contained 18% of nitrogen, and was probably impure ammonium phenylbarbiturate (N, 19%). Ammonium barbiturate is formed in the analogous reaction with malonyl-diurethane (3).

With Ethylamine. Three grams of the diurethane was treated with 25% aqueous ethylamine for a week at room temperature. Large branching crystals separated; m.p. 154° C. It was apparently phenylmalon-diethylamide. Yield, 60%. Calc. for $C_{13}H_{18}N_2O_2$: N. 11.96%. Found: N, 11.67%. The filtrate was evaporated and the residue extracted with ether and alcohol. The extract yielded urethane. The small insoluble residue was not absolutely identified, but it was probably the impure ethylamine salt of phenylbarbituric acid (see preceding section). Calc. for $C_{12}H_{15}N_3O_3$: N, 16.8%. Found: N, 16.3%.

With Aniline (at 150° C.). Two grams of diurethane was heated with 9.5 gm. of aniline for two hours at 150° C. Fine crystals separated on cooling. Ether was added and the mixture filtered. The ether insoluble portion melted at 204° to 205°. It was undoubtedly phenylmalonanilide. The yield was 28%. Calc. for $C_{21}H_{18}N_2O_2$: N, 8.48%. Found : N, 8.27, 8.39%. The ethereal filtrate was evaporated until crystals appeared. The product was recrystallized from hot alcohol; m.p., 234° to 235°. It was apparently phenylmalonyldi-(phenylurea). Calc. for $C_{23}H_{20}N_4O_4$: N, 13.46%. Found:

N, 12.97, 12.89%. When this product was heated with aniline for one hour at 150° to 160° it was converted completely to phenylmalonanilide and diphenylurea.

The ether filtrate was completely evaporated to dryness. The residue was separated by fractional crystallization into diphenylurea (m.p. 236° C.) and a small quantity of substance melting at 151°. This was probably phenylureido-phenylmalonyl-urethane (IV)*. Calc. for $C_{19}H_{19}N_3O_5$: N, 11.38%. Found: N, 10.85, 10.94%.

With Aniline (at 180° to 190°). Two grams of the diurethane was heated with 9.5 gm. of aniline at 180° to 190° for two hours. The semisolid mass obtained was treated with ether and filtered. The crystalline product was identified as phenylmalonanilide. From the filtrate, diphenylurea was obtained. A small gummy residue was left but no other crystalline products were obtained.

Reactions of Phenylsuccinyl-diurethane

With Ammonia. Two grams of the diurethane was treated with 25% ammonia for a week at room temperature. The crystalline product that separated was identified as phenylsuccinamide. Calc. for $C_{10}H_{12}N_2O_2$: N, 14.58%. Found: N, 14.50%. The ammoniacal filtrate yielded urethane.

With Ethylamine. By a procedure similar to the above, using aqueous ethylamine, a 60% yield of phenylsuccinyl-diethylamide was obtained; m.p., 179° to 180°. Calc. for $C_{14}H_{17}N_2O_2$: N, 11.10%. Found: N, 11.42%. The filtrate yielded urethane.

With Aniline (1) at 180° C. The diurethane (1.5 gm.) and aniline (8 gm.) were heated for two hours at 180° C. The viscous mass was taken up in ether. A crystalline product was filtered off. It was washed with ether to remove gum and recrystallized from alcohol; m.p. 235°. It was apparently phenylsuccinyldi-(phenylurea) and was the main product of the reaction. Calc. for $C_{24}H_{22}N_4O_4$: N, 13.02%. Found: N, 12.80, 12.86%. From the ether filtrate a small amount of diphenylurea was obtained; this indicated some splitting of urethane from the original compound. There was considerable formation of unresolvable gum.

With Aniline (2) at 180° to 200° C. One gram of the diurethane was heated with 5 gm. of aniline for three hours at 180° to 200°. Phenylsuccinyldi-(phenylurea) was again obtained (0.3 gm.). The ether filtrate on evaporation yielded a small amount of flocculent material. This was recrystallized from alcohol. It melted at 234° but was not the diurea. It was apparently phenylureido-phenylsuccinanilide, a decomposition product of the diurea. Calc. for $C_{23}H_{21}N_3O_3$: N, 10.85%. Found: N, 11.00, 11.14%. From the final gummy residue, diphenylurea was obtained.

---

* *Phenylureido-phenylmalonanilide has a nitrogen content of 11.26% but it is almost certain that this substance would have a much higher melting point, probably in the region of 230° to 235°. It was expected that this compound would be formed but no appreciable quantity was isolated.*

Reaction of Malonyl-diurethane with Cyclohexylamine

Diurethane (2 gm.) was refluxed with 30% aqueous cyclohexylamine for a short time. A white crystalline substance separated when the solution cooled; m.p. 174° C. Yield, 0.64 gm. It was malon-di-cyclohexylamide. Calc. for $C_{15}H_{26}N_2O_2$: N, 10.52%. Found: N, 10.49, 10.52%. From the evaporated filtrate a gummy mass was obtained which yielded urethane by extraction with ether.

References

1. BASTERFIELD, S. and TOMECKO, J. W. Can. J. Research, 8(5) : 458-462. 1933.
2. BASTERFIELD, S., WILSON, C. V., and GREIG, M. E. Can. J. Research, 4(4) : 361-371. 1931.
3. BASTERFIELD, S., WOODS, E. L., and WHELEN, M. S. J. Am. Chem. Soc. 49(11) : 2942-2948. 1927.
4. DOX, A. W., and YODER, L. J. Am. Chem. Soc. 44(7) : 1564-1567. 1922.

THE ADEQUACY OF VITAMIN C IN ALBERTA DIETS[1]

By Hilda K. Waagen[2] and L. B. Pett[3]

Abstract

A survey was carried on for 12 months to determine the amount of vitamin C actually available in the food served in Athabasca Hall, a residence for men at the University of Alberta. The amount of vitamin C excreted by some of the persons living at Athabasca Hall was also determined and correlated with the intake. It was found that the output was higher in the fall after high intake than in the spring after the low supply during the winter. The average daily intake of vitamin C from November to May, inclusive, was 41 mg., and from June to October, inclusive, 82 mg. If citrus fruits had been excluded from the diet, the intake would have been markedly less. In the spring months the tissues of all persons tested by a test dose method were found to be unsaturated, whereas in the autumn two persons out of six showed tissue saturation. No frank scurvy existed among the subjects and no marked incidence of gum-bleeding was reported.

Introduction

Attention has been focused by many investigators on determining whether the amount of vitamin C excreted in the urine has a fixed, definite relation to the vitamin C requirements of the body. It has been confirmed that the amount of ascorbic acid excreted in the urine is dependent on the degree of tissue saturation (9, 10, 16), which in turn is dependent on the previous diet. The quantity excreted varies so greatly even with the same individual that it is difficult to state in arbitrary figures a normal value for all people (9). Spellberg and Keeton (16), after a survey of the literature, placed the minimum normal amount excreted at 20 mg. in 24 hr. Harris *et al.* (8) noted that the normal daily output remained fairly constant at 30 to 33 mg., but in later work (1) they state 20 mg. per day to be the rate of excretion on a moderately low intake, and that 10 to 15 mg. per day represents the borderline group. However, Evelyn, Malloy, and Rosen (6) have found with the photoelectric colorimetric method that apparently normal healthy individuals have a 24 hr. output of 5 mg. or less. Thus there is some doubt in interpreting the rate of urinary output of vitamin C as an indication of dietary adequacy of the vitamin.

Many people consider that tissue saturation is better evidence of dietary adequacy of vitamin C. It is determined by titration of urine samples, before and after the administration of test doses. The percentage output of the dose in 24 hr. is low if the tissues are unsaturated, and if they are fully saturated, 60 to 80% will be excreted (2). Excretion of 50% or more of

---

[1] *Manuscript received in original form August 28, 1942, and as revised, September 1, 1942.*
Contribution from the Department of Biochemistry, University of Alberta, Edmonton, Alta., with financial assistance derived from a grant to Prof. G. Hunter from the Associate Committee on Medical Research of the National Research Council of Canada. This work was included in a thesis for the degree of Master of Science in the University of Alberta.

[2] *Formerly Research Assistant, 1939–41.*

[3] *Director of Nutrition Services, Department of Pensions and National Health, Ottawa. At the time, Lecturer in Biochemistry, University of Alberta.*

the test dose can be taken as an indication of tissue saturation (15). On the basis of these tests the daily requirement for vitamin C has been placed as high as 100 mg.

Although these determinations give some knowledge regarding the saturation of the tissues, it is doubtful whether saturation is necessary for optimal health. Rietschel and Mensching (13) experimented with a vitamin-C–free diet, on which one of them lived for 100 days without manifestation of prescorbutic symptoms. He appeared quite as healthy at the end of the test period as he had at the beginning, although the level of vitamin C in the blood and the amount excreted in the urine were virtually zero. These authors state that a daily intake of 15 mg. may be adequate.

It is apparent that the literature on vitamin C contains many differing results and opinions so that at the present time no agreement exists regarding the best method of determining vitamin C adequacy. In the past three years, the tendency has been to assume, without adequate clinical evidence, that tissue saturation is essential. The final solution of the problem demands further clinical work. However, most investigators agree that more than the minimum preventive dose should be taken daily.

This and similar questions regarding other vitamins can be finally answered only by studying groups of people on controlled intakes of the vitamin, determined by analyses. Much work remains to be done on these problems.

As described in this paper, the authors have determined in average figures the actual daily consumption of vitamin C by persons subsisting on an ordinary, well balanced diet. They also determined the output of the vitamin by some of these persons, in order to correlate the daily intake with the amount excreted. This work is of importance not only as the first of its kind in Western Canada, but also as a contribution to the general problem of human requirements for vitamin C.

Experimental

For one week in each of 12 months, from December, 1939, to December, 1940, the vitamin C contents of foods served in Athabasca Hall, a residence for male students of the University of Alberta, were determined. The kitchens supply food for approximately 400 students. When possible, all vegetables are cooked with steam; fruits are stewed. Thus, it was assumed that the meals served there would be fairly representative of better class or well supervised, large-scale selection and preparation of foods.

In summer, most of the vegetables were obtained fresh from the University gardens; in the winter, stored vegetables, such as potatoes, carrots, turnips, cabbage, etc., and canned vegetables, such as peas and beans, were used. The oranges, apples, grapefruit, and bananas were fresh or stored, depending on the season during which they were obtained. In the winter, any fruits other than the above mentioned were canned (peaches, pears, plums, pineapple), whereas in the summer other fresh fruits, such as peaches, plums, raspberries, and strawberries, were obtainable.

During the apple season, more of this fruit was served than any other. In the summer months of July, August, and September, apples were omitted, oranges being the main fruit; occasionally the latter were replaced by cherries, peaches or grapes.

The results are calculated on servings of the following amounts: vegetables and stewed fruits—100 gm.; oranges, apples, peaches—one fruit; grapefruit—one-half.

The ascorbic acid was estimated in any fresh fruit served at breakfast, and in the vegetables and fruits served at dinner and supper. It was not determined in meats as the amount of vitamin C contained in meat after cooking is considered to be negligible (14). Soups and milk were not tested (5 mg. of vitamin C in one pint of milk (3)).

The estimations were carried out during the first complete week of each month (Monday to Saturday). Actual determinations of ascorbic acid in the food served on Sunday were not made, but the amount was calculated from the values obtained on the preceding six days.

The procedure adopted was a modification of the 2,6-dichlorophenol-indophenol titration method (7). The extracting acid was a 2% solution of metaphosphoric acid in 2 *N* hydrochloric acid. This mixture had no appreciable effect on the dye; no decolorization took place until three or four minutes had elapsed. The dye solution was run from a 10 ml. microburette into 5 ml. of the hydrochloric-metaphosphoric acid extract of the tissue under examination. A pink colour that persisted for 10 sec. was taken as the end-point of the titration.

The preparation of the acid extract was similar to the methods used by Pett (12) and by Thornton (17). A sample, obtained by quartering, was weighed (20 gm.), immediately placed in a beaker, and covered with the acid mixture. It was then ground in a mortar, with sand if necessary, to a fairly fine pulp. The grinding was not prolonged beyond the minimum time necessary. The mixture was then poured into a graduated cylinder, the mortar and beaker were rinsed with acid solution, and the washings added to the contents of the cylinder. The final volume was made up to 80 ml. The mixture was allowed to stand a few minutes, with occasional shaking, and it was then filtered into a beaker containing a pinch of zinc dust. The zinc reacts with the hydrochloric acid and the hydrogen evolved reduces any dehydro-ascorbic acid to ascorbic acid. The zinc was allowed to react for three to five minutes, or until the foam subsided. When potatoes, or any creamed or very starchy vegetables are being tested, it is better to centrifuge the mixture in order to obtain a clear extract.

The McHenry and Graham (11) modified method for the titration of deeply coloured extracts was used when necessary.

The indophenol dye solution was standardized against a solution of known ascorbic acid content. The phosphate buffer (pH 7.2) used in preparation of the dye solution stabilized it sufficiently that restandardization was necessary only every two weeks. The strength was such that 1 cc. was approximately equivalent to 0.200 mg. of ascorbic acid.

Reduction of dehydro-ascorbic acid was effected by means of zinc in preference to hydrogen sulphide (5, 4), as it is the more rapid procedure. It is possible that zinc will reduce other substances so that they will also reduce the dye. Experiments with raw potato extract showed that three to five minutes was sufficient time for the reduction by zinc.

The method was further tested for reliability and was found to be satisfactory. The results obtained were essentially the same as Thornton's (17).

Tests on Urinary Output of Ascorbic Acid

Estimations of vitamin C in the urine of several residents were carried out for the purpose of correlating the output of vitamin C with the dietary intake. This was done in the latter part of January, 1940, and again in the latter part of September, 1940. During the summer the subjects were not all in continuous residence at Athabasca Hall.

The amount of ascorbic acid excreted was determined on one day and again on the next day after the administration of a 200 mg. test dose of pure ascorbic acid. The tests were carried out on 24 hr. specimens, collected in brown bottles, and preserved with a mixture of 5 ml. of 20% metaphosphoric acid and 15 ml. of concentrated hydrochloric acid. The titrations were done on the day of the final collection for the 24 hr. period.

The method used for the estimation of vitamin C in urine was a modification of that of Abbasy, Harris, *et al.* (1). The dye solution was a 1 : 10 dilution of that used for the plant titrations; 1 ml. = approximately 0.020 mg. of vitamin C. It was restandardized after dilution. This dilution of the dye is stable for not more than two days. It was run in from a 10 ml. burette into 5-ml. urine samples (diluted with 10 ml. of hydrochloric-metaphosphoric acid mixture) until a definite pink colour persisted for 10 sec.

An average percentage recovery of 96.5 of added ascorbic acid was obtained by this method. If, instead, the urine was run into a known quantity of dye, inconsistent results and low percentage recoveries were obtained. This error was due to the presence of other reducing substances in the urine, which have a greater opportunity to react with the dye.

Results

For 12 months the diet of residents of Athabasca Hall was investigated. The bar graph (Fig. 1) shows clearly the variation per month in intake, and the effect that removal of citrus fruits (grapefruit and oranges) from the diet would have.

For the months from November to May, inclusive, the average daily intake was found to be 41 mg. From June to October, inclusive, it was 82 mg.

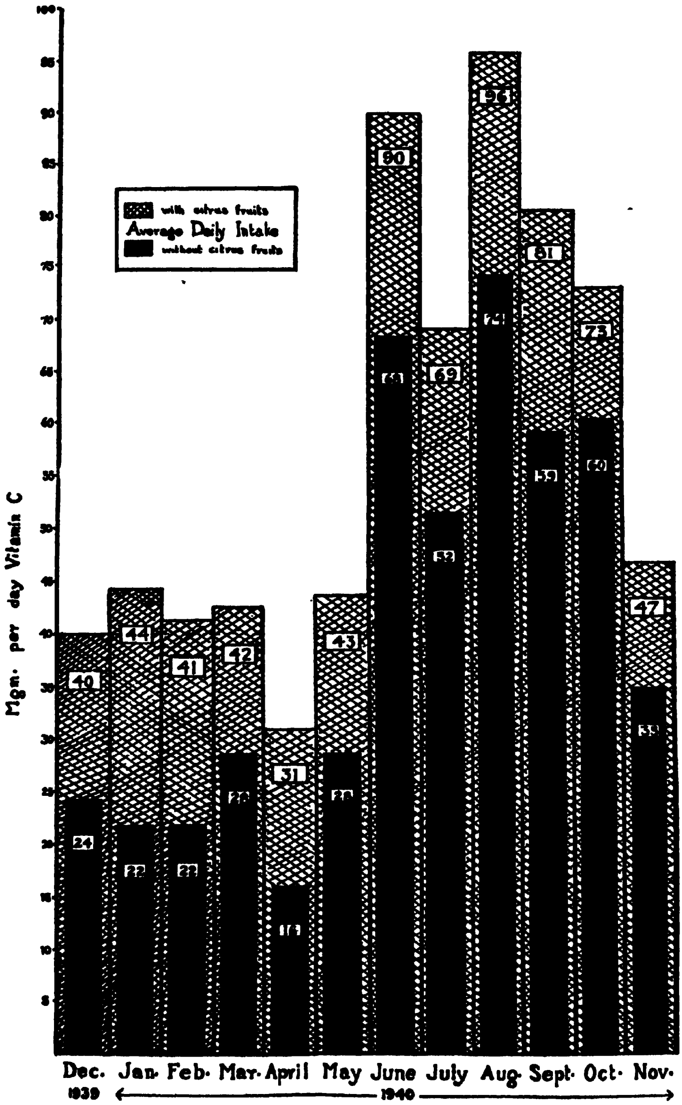


FIG. 1. *Average daily intake of vitamin C, Athabasca Hall dietary.*

The intake of vitamin C in June is high, because of the abundant supply of fresh strawberries. The value for July is 21 mg. less, but is still high because of the fresh tomatoes and other fresh vegetables then coming into use. The highest intake is in August, owing to the increased vitamin C content of potatoes, cabbage, cauliflower and tomatoes, the vitamin C content of which is then about at its peak. The intake in September and October drops slightly, and November shows a definite decline, owing mainly to loss of ascorbic acid in vegetables on storing and the omission of fresh and canned tomatoes during the week of the test. In April the lowest values for potatoes and oranges were recorded, and no tomatoes were eaten during the week, all of which accounts partly for the daily intake being the least in April.

Urinalysis Results

The results obtained by different workers on the output of vitamin C as related to dietary intake and saturation of the tissues are many and varied (15). Abbasy *et al.* (1) state that an excretion of 10 to 15 mg. vitamin C in 24 hr. indicates a borderline intake, while Van Eekelen *et al.* (18) state that 40 mg. output per day indicates a liberal intake and saturation of the tissues. Johnson and Zilva (9) found that the excretion of vitamin C in the winter is almost nil, never greater than 10 to 15 mg. a day; but it rose after the summer.

In January the average amount excreted was 17 mg. a day (Table I). In Table II, although the average is 14.3 mg. per day, only one output falls below 10 mg. and four of the seven exceed 15 mg. In Table III, however, the average amount excreted by students tested in March was only 7.4 mg. This

TABLE I

URINARY OUTPUT OF VITAMIN C BY ATHABASCA HALL RESIDENTS

Subject	Vitamin C excreted, mg./24 hr.		
	Before test dose	After test dose	Per cent excreted*
January 20 – 21, 1940			
E.O.L.	20.9	15.6	0.0
L.T.	17.8	17.6	0.0
L.B.P.	15.1	21.0	3.0
E.H.B.	16.3	24.6 (after 400 mg. dose)	2.1
J.H.W.	17.1	17.3	0.1
W.W.P.	14.8	18.6	1.9
Average	17.0	19.1	1.05
September 27 – 28, 1940			
E.O.L.	23.2	65.9	21.4
L.T.	54.8	195.1	70.2
L.B.P.	27.4	23.3	0.0
E.H.B.	42.6	117.8	37.6
J.H.W.	43.7	86.4	21.4
W.W.P.	23.7	37.3	6.8
Average	35.9	87.6	25.9

* *The percentage excreted is calculated as follows:*

$$\frac{\textit{Test dose output} - \textit{normal output}}{\textit{Test dose (200 mg.)}} \times 100 = \%\ \textit{excreted.}$$

TABLE II

URINARY OUTPUT OF VITAMIN C BY MALE SUBJECTS TESTED ONLY IN JANUARY

January 23 – 24, 1940

Subject	Vitamin C excreted in mg./24 hr.		
	Before test dose	After test dose	Per cent excreted
J.L.	12.0	66.5	27.3
A.C.G.	18.4	40.6	11.1
H.	7.9	16.6	4.4
F.D.	18.4	19.6	0.6
A.E.R.	15.1	16.2	0.6
F.W.	11.1	11.4	0.2
A.C.W.	16.9	13.4	0.0
Average	14.3	26.3	6.0

TABLE III

URINARY OUTPUT OF VITAMIN C IN MG./24 HR.

March 14, 1940		December 5, 1940
Normal output level, Group I	Output after 200 mg. test dose, Group II	Normal output level, Group III
2.6	2.4	8.7
3.3	3.7	12.5
3.4	4.3	15.0
3.9	4.6	15.2
4.3	5.0	15.4*
5.1	6.6	15.5
5.3	6.8	16.8
5.4*	7.1	16.9
5.4	7.1	17.0
5.4	7.7	17.1
5.4	8.2	17.3
5.9	8.9*	17.4
6.2	10.2*	18.0
6.4*	10.3	18.3
6.4	14.2*	18.7
6.8	14.7	19.1
7.0	16.3	19.6
8.4*	36.0	19.6
8.5	46.6	19.8
8.7*	70.8	20.1
8.7	73.7	20.2
9.0	86.0	20.8
9.0	93.8	21.7
12.2		23.6
12.3		24.8
12.6		27.0*
24.6		27.5
		29.1
Average 7.4 mg./day	23.7 mg./day	19.1 mg./day

* *Residents of Athabasca Hall.*

drop in average output from January to March may be accounted for in part by individual variation, but would more likely be due to decreased intake (Fig. 1) and gradual depletion of the body stores.

Even after a 200 mg. test dose, Group II showed an average output of only 23.7 mg. per day, that of 73.9% of the subjects being below this average figure.

The state of saturation of the tissues is indicated more clearly by the output after a test dose. Baumann (2) estimated that 60 to 80% of the test dose will be excreted in 24 hr. by a healthy person whose tissues are saturated. In January (Tables I and II) these figures are not nearly approximated. September however presents a better picture, with the average output before the test dose doubled, that after the test dose four times greater, and the average percentage of vitamin C excreted many times increased. Even so, only L.T. and E.H.B. come within range of percentage output estimated by Baumann, taking into consideration that Baumann estimates the percentage on total output figures, not on the difference between the output level before and after the test dose.

In December (Table III) the average amount excreted by Group III is 19.1 mg.—three times the output in March. This is indicative of increased body stores, as are the higher outputs obtained in September. As can be seen from the tables, the total and percentage output vary greatly with the different individuals. The 200 mg. ingested by L.B.P. (Table I) was, then, either absorbed and taken up by the tissues or was destroyed in the gastro-intestinal tract. Blood analyses would indicate which of these processes actually occurred. Similar examples can be found in Table II. It seems evident that different individuals have different saturation capacities, and that an estimation of the normal output cannot always be a true indication of the saturation of the tissues. Determination of the output after a test dose is a better means of determining saturation. However, a single estimation of urinary vitamin C is valuable in distinguishing extreme deficiency. It is also useful in a survey of adequacy in a large group of persons.

Discussion

From the tables presented it can be seen that the tissues of persons subsisting on a diet that supplies an average daily intake of 41 mg. of vitamin C per day are not nearly saturated, according to the data obtained in determining output after a test dose. As this intake is increased to an 82 mg. average, the amount excreted also increases in simple relation, but only two persons out of six showed saturation. If tissue saturation is the true criterion of optimum vitamin C utilization, then it seems that even the well supervised, large-scale cooking methods studied here do not supply an adequate amount of vitamin C. Also, if tissue saturation measured by a test dose of 200 mg. is the criterion, the daily requirement must be very high.

Acknowledgments

The writers' indebtedness is expressed to Dr. G. Hunter for his interest; to Miss R. Eager for access to the kitchens of Athabasca Hall; and to the subjects.

References

1. Abbasy, M. A., Harris, L. J., Ray, S. N., and Marrack, J. R. Lancet, 229 : 1399-1405. 1935.
2. Baumann, T. Klin. Wochschr. 16 : 1246-1248. 1937. *Quoted by* Smith (15).
3. Bessey, O. A. J. Am. Med. Assoc. 111 : 1290-1298. 1938.
4. Bessey, O. A. J. Biol. Chem. 126(3) : 771-784. 1938.
5. Emmerie, A. and Van Eekelen, M. Biochem. J. 28 : 1153-1154. 1934.
6. Evelyn, K. A., Malloy, H. T., and Rosen, C. J. Biol. Chem. 126(3) : 645-654. 1938.
7. Harris, L. J. and Ray, S. N. Biochem. J. 27 : 303-310. 1933.
8. Harris, L. J., Ray, S. N., and Ward, A. Biochem. J. 27 : 2011-2015. 1933.
9. Johnson, S. W. and Zilva, S. S. Biochem. J. 28 : 1393-1408. 1934.
10. Kellie, A. E. and Zilva, S. S. Biochem. J. 33 : 153-164. 1939.
11. McHenry, E. W. and Graham, M. Biochem. J. 29 : 2013-2019. 1935.
12. Pett, L. B. Biochem. J. 30 : 1228-1232. 1936.
13. Rietschel, H. and Mensching, J. Klin. Wochschr. 18 : 273-278. 1939.
14. Sherman, H. C. and Smith, S. L. The vitamins. Am. Chem. Soc. Monograph No. 6. 2nd ed. Chemical Catalog Company, Inc., New York. 1931. *As quoted by* Bessey (3).
15. Smith, S. L. J. Am. Med. Assoc. 111 : 1753-1764. 1938.
16. Spellberg, M. A. and Keeton, R. W. Arch. Internal Med. 63 : 1095-1116. 1939.
17. Thornton, N. C. Contrib. Boyce Thompson Inst. 9(4) : 273-281. 1938.
18. Van Eekelen, M., Emmerie, A., and Wolff, L. K. Z. Vitaminforsch. 6 : 150-162. 1937. *Quoted by* Smith (15).

THE REACTION OF HYDROGEN ATOMS WITH ISOBUTANE[1]

W. HAROLD WHITE[2], C. A. WINKLER[3], AND B. J. KENALTY[4]

Abstract

The reaction of hydrogen atoms with isobutane has been investigated by the Wood–Bonhoeffer discharge tube method, over a temperature range 30° to 250° C. An activation energy of 10.5 ± 1.5 kcal. was obtained for the reaction.

The nature of the products at a given temperature was found to depend upon the concentration of hydrogen atoms present. With low atom concentrations (5 to 9%) methane was essentially the only product at temperatures below 170° C. At 250° C., ethane was formed to the extent of approximately one-half the amount of methane. With higher atom concentrations (14 to 24%) ethane was formed in appreciable quantities at 140° to 170° C., and exceeded the methane content at 250° C. Small amounts of propane were formed at the higher temperatures.

The results at low temperatures appear to be satisfactorily explained by assuming a primary dehydrogenation reaction:

$$i\text{-}C_4H_{10} + H \longrightarrow C_4H_9 + H_2 ,$$

followed by a series of "atomic cracking" reactions. To account for the behaviour at higher temperatures, additional secondary reactions, involving decomposition of radicals and their reaction with molecular hydrogen, are assumed.

Introduction

Reactions between hydrogen atoms and the lower normal paraffin hydrocarbons have been studied extensively. It is assumed generally that the primary step is abstraction of a hydrogen atom from the hydrocarbon molecule, followed by a series of "atomic cracking" reactions. Thus, the reactions postulated for normal butane (12) are:

$$H + C_4H_{10} \longrightarrow C_4H_9 + H_2 ,$$

followed at low temperatures by:

$$\begin{aligned} H + C_4H_9 &\longrightarrow C_3H_7 + CH_3 \\ &\longrightarrow 2C_2H_5 \\ H + C_3H_7 &\longrightarrow C_2H_5 + CH_3 \\ H + C_2H_5 &\longrightarrow 2CH_3 \\ H + CH_3 &\longrightarrow CH_4 . \end{aligned}$$

At higher temperatures, additional secondary reactions are assumed.

No investigation of the reaction between hydrogen atoms and isobutane has been reported previously. A study of this reaction was of interest, not only to obtain additional information about the elementary reactions of the hydrocarbons in the presence of hydrogen atoms, but also to enable comparison of the behaviour of a branched chain molecule with that of the straight chain hydrocarbons previously investigated.

---

[1] *Manuscript received July 20, 1942.*

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Postgraduate student, McGill University, and holder of a Fellowship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry, McGill University.*

[4] *Postgraduate student and Demonstrator in Chemistry, McGill University.*

Experimental

The reaction was studied by the Wood–Bonhoeffer method, in an apparatus similar essentially to that described previously by Steacie (11).

Commercial hydrogen was purified by passage over platinized asbestos at 500° C., through a drying tube and a liquid-air cooled trap to remove water and finally through a trap containing silica gel cooled in liquid air to remove traces of methane found to be present. This dry hydrogen was used in several experiments. In others, the purified gas was moistened by passage over water in a trap at room temperature. The hydrogen was admitted to the reaction vessel through a calibrated flowmeter, the pressure at the inlet of the flowmeter being maintained at atmospheric by a mercury blow-off valve.

Isobutane was obtained from the Ohio Chemical and Manufacturing Company. It was specified to be 99% pure, with *n*-butane the only impurity. It was used after a single low-temperature fractionation. The isobutane flow rate was regulated by adjusting the pressure on the supply side of a capillary flowmeter.

Hydrogen atoms were formed in a high voltage discharge tube, consisting of a Pyrex tube, 2.5 cm. in diameter, to which were sealed two side tubes each containing an aluminium electrode. Connection to the electrodes was made with heavy platinum wires which passed out of the electrode chambers through capillary tubes and DeKhotinsky seals. The discharge was operated with 2500 volts across the tube and a 5000 ohm resistance. The operating current was kept at 200 milliamperes by a rheostat in the primary circuit of the transformer.

The reaction chamber was a Pyrex tube 7 cm. in diameter, with a volume of 895 ml. It was situated close to the discharge to minimize hydrogen atom recombination prior to reaction. The chamber was surrounded by an electric furnace, the temperature of which was manually controlled to within 2° C. The isobutane inlet tube and a thermocouple well were sealed into the reaction vessel from below.

The wall of the reaction chamber was poisoned with phosphoric acid to enable a suitable concentration of hydrogen atoms to be maintained with a stream of dry hydrogen. When moist hydrogen was used, the additional poisoning action gave an atom concentration two to three times that secured with dry hydrogen.

The products of reaction, together with unchanged isobutane and hydrogen, were drawn from the reaction vessel by a high-speed diffusion pump backed by an oil pump. The reaction time was varied between 0.40 and 0.91 sec. A liquid-air cooled trap between the reaction vessel and the diffusion pump served to remove unchanged isobutane, higher hydrocarbons if present, and the major portion of any propane, ethane, or ethylene. The remainder of the gas stream passed through the diffusion pump and through a liquid-air cooled trap containing silica gel to remove methane.

After each experiment, which lasted 2–2.5 hours, the reaction products were removed to a gas holder and analysed on a low temperature distillation unit of the Podbielniak type. The hydrogen–methane fraction was analysed by combustion. In addition to the distillation, the content of unsaturates in some samples was determined by absorption in a bromine–potassium-bromide solution.

The hydrogen atom concentration in the reaction vessel was measured at each working temperature with a Wrede diffusion gauge. The pressure differential set up by atom recombination in the capillary of this instrument was determined with a Pirani gauge. The values obtained for the hydrogen atom concentration would be higher than those existing during an experiment when the concentration of atoms is reduced by reaction. Correction was made for a pressure differential in the gauge, arising from thermal effects, by making measurements at each temperature without the discharge tube in operation.

Results

The experimental conditions employed and the analytical data obtained are given in Table I.

The number of collisions per second of an isobutane molecule with hydrogen atoms was calculated from the expression (7, p. 46):

$$Z_{C_4H_{10}\cdot H} = 2\sqrt{2\pi}\left(\frac{d_H + d_{C_4H_{10}}}{2}\right)^2\left(\frac{M_H + M_{C_4H_{10}}}{M_H \cdot M_{C_4H_{10}}}\cdot RT\right)^{\frac{1}{2}} \cdot N_H,$$

where d_H and $d_{C_4H_{10}}$ are the molecular diameters,

M_H and $M_{C_4H_{10}}$ are the molecular weights,

N_H is the number of hydrogen atoms per ml.,

and R and T are the gas constant and the absolute temperature respectively. The value of d_H was taken as 2.14×10^{-8} cm. (1) and that of $d_{C_4H_{10}}$ as 4.66×10^{-8} cm. (18).

The activation energies were calculated from the relation

$$\text{Collision yield} = A.e^{-E/RT},$$

assuming a value of 0.1 for the steric factor, A. This steric factor, while possibly too large (6, 8), was taken to facilitate comparison between the results of this investigation and others of a similar type, where the value 0.1 has been used.

The data necessary for the calculation of the activation energies and the values obtained are given in Table II.

Discussion

Comparison of the collision yields for isobutane with those for normal butane (12) shows that the hydrogen atom reaction with isobutane is of the order 10 times slower than that with normal butane (Table II). In fact, the rate of the isobutane reaction is approximately the same as that of propane (13). Apparently, the branched chain of isobutane offsets any tendency

TABLE I

EXPERIMENTAL CONDITIONS AND PRODUCTS FORMED IN THE REACTION OF ISOBUTANE WITH HYDROGEN ATOMS

Run. No.	Temp., ° C.	Press., mm.	Atom conc., %	Condition of hydrogen	Flow, moles/sec. × 10^5		Products, mole %				Butane reacted, %
					H_2	C_4H_{10}	CH_4	C_2H_6	C_3H_8	C_4H_{10}	
1	32	0.36	9.1	Dry	1.54	0.245	11.9	—	—	88.1	3.4
2	31	0.36	9.1	Dry	1.54	0.250	11.7	—	—	88.3	3.2
3	32	0.36	9.1	Dry	1.54	0.246	12.7	—	—	87.3	3.5
4	32	0.33	24.2	Moist	1.82	0.434	7.1	Trace	Trace	92.9	1.9
5	33	0.33	24.2	Moist	1.82	0.450	7.2	Trace	Trace	92.8	1.9
6	101	0.36	8.2	Dry	1.54	0.239	12.0	—	—	88.0	3.3
7	101	0.36	8.2	Dry	1.54	0.247	11.0	—	—	89.0	3.0
8	100	0.36	8.2	Dry	1.54	0.245	13.9	—	—	86.1	3.9
9	101	0.36	8.2	Dry	1.54	0.245	14.0	—	—	86.0	3.9
10	101	0.36	8.2	Dry	1.54	0.239	13.7	—	—	86.3	3.8
11	141	0.32	17.3	Moist	1.82	0.445	6.2	0.7	Trace	93.1	2.0
12	140	0.32	17.3	Moist	1.82	0.440	5.3	0.6	Trace	94.1	2.0
13	171	0.36	7.1	Dry	1.54	0.251	13.7	Trace	Trace	86.3	3.8
14	171	0.36	7.1	Dry	1.54	0.245	13.5	Trace	Trace	86.5	3.8
15	172	0.36	7.1	Dry	1.54	0.245	12.9	Trace	Trace	87.1	3.6
16	171	0.36	7.1	Dry	1.54	0.249	13.4	Trace	Trace	86.6	3.7
17	170	0.32	7.1	Dry	1.82	0.220	4.8	Trace	Trace	95.2	1.6
18	170	0.32	16.0	Moist	1.82	0.218	5.2	3.6	1.1	90.1	4.2
19	250	0.33	5.6	Dry	1.82	0.225	7.4	3.7	—	88.9	4:0
20	250	0.34	13.9	Moist	1.82	0.408	6.5	9.0	1.8	82.7	8.5
21	250	0.35	13.9	Moist	1.82	0.417	6.4	8.0	1.8	83.8	7.6
22	250	0.32	13.9	Moist	1.82	0.242	12.4	14.9	Trace	72.7	12.6

TABLE II

DATA FOR COLLISION YIELDS AND ACTIVATION ENERGIES IN THE REACTION OF ISOBUTANE WITH HYDROGEN ATOMS

Run No.	Temp., ° C.	Total flow corrected for hydrogen atoms, moles/sec. $\times 10^5$	Reaction time, sec.	Partial press. of hydrogen atoms, mm.	$Z_{C_4H_{10} \cdot H}$ per sec. $\times 10^{-5}$	$Z_{C_4H_{10} \cdot H}$ in reaction time $\times 10^{-5}$	Butane reacted, %	Collision yield $\times 10^8$	E, kcal, assuming $A = 0.1$
1	32	1.86	0.91	0.033	9.73	8.84	3.4	3.85	9.0
2	31	1.86	0.91	0.033	9.73	8.84	3.2	3.62	9.0
3	32	1.86	0.91	0.033	9.73	8.84	3.5	3.96	8.9
4	32	2.47	0.63	0.080	23.6	14.8	1.9	1.28	9.6
5	33	2.49	0.62	0.080	23.5	14.6	1.9	1.30	9.6
6	101	1.84	0.75	0.029	7.47	5.62	3.3	5.88	10.7
7	101	1.85	0.75	0.029	7.47	5.62	3.0	5.34	10.7
8	100	1.85	0.75	0.029	7.47	5.62	3.9	6.94	10.6
9	101	1.85	0.75	0.029	7.47	5.62	3.9	6.94	10.6
10	101	1.84	0.75	0.029	7.47	5.62	3.8	6.76	10.6
11	141	2.42	0.46	0.055	14.0	6.44	2.0	3.10	12.3
12	140	2.42	0.47	0.057	14.5	6.86	2.0	2.92	12.3
13	171	1.85	0.63	0.025	5.52	3.50	3.8	10.8	12.1
14	171	1.84	0.63	0.025	5.52	3.50	3.8	10.8	12.1
15	172	1.84	0.63	0.025	5.52	3.50	3.6	10.3	12.2
16	171	1.84	0.63	0.025	5.52	3.50	3.7	10.6	12.2
17	170	2.10	0.49	0.023	5.56	2.74	1.6	5.84	12.7
18	170	2.18	0.48	0.051	12.5	5.95	4.2	7.06	12.5
19	250	2.10	0.43	0.018	4.17	1.81	4.0	22.1	13.5
20	250	2.35	0.40	0.048	10.7	4.26	8.5	20.0	13.7
21	250	2.36	0.41	0.049	11.0	4.47	7.6	17.0	13.8
22	250	2.19	0.40	0.044	10.0	4.03	12.6	31.3	13.2

towards increased reactivity with increasing molecular weight (4, 19), such as is observed between propane and normal butane.

The values of the activation energy of the isobutane reaction are higher than those found for normal butane at corresponding temperatures (Table II). It may be assumed that at least part of the observed increase of activation energy with increased temperature is only apparent, and is the result of error in the assumed atom concentration at higher temperatures where the increased amount of reaction might be expected to cause a relatively greater lowering of the stationary hydrogen atom concentration. Part of the increase in E might, however, be the result of a decreased steric factor brought about, for example, by increased rotation of the molecule, or increased oscillation of alkyl groups at the higher temperatures. Giving somewhat greater weight to the lower temperature values, the activation energy for the reaction of hydrogen atoms with isobutane may be taken as 10.5 ± 1.5 kcal.

The relative amounts of ethane and methane at a given temperature, at the higher temperatures, were dependent upon whether dry or moist hydrogen was used (Table I). Using dry hydrogen, only traces of ethane were found at temperatures up to 170° C., and the methane content exceeded the ethane at 250° C. Using moist hydrogen, the amount of ethane became appreciable between 140° to 170° C., and surpassed the methane content at 250° C. If, as seems highly probable (3, p. 153, 11), the only significant effect of using moist hydrogen is to increase the hydrogen atom concentration, the results indicate clearly that the nature of the products at a given temperature in discharge tube studies may depend largely upon the hydrogen atom concentration.

These data may be compared with the results reported for the same reaction with normal butane (12). At 35° C., normal butane yielded methane exclusively, with appreciable quantities of ethane appearing when the temperature was raised to 100° C. The ratio of ethane to methane increased rapidly with increasing temperature until at 250° C. there was approximately twice as much ethane as methane in the products. Analysis showed that propane was not produced at any temperature.

Thus the behaviour of isobutane using moist hydrogen, i.e., at the higher atom concentrations, is analogous to that reported for normal butane using dry hydrogen and with atom concentrations considerably smaller than those obtained in the present study under similar conditions. This fact was thought at first to indicate a marked difference between the two reactions. An experiment was therefore made with normal butane, at 32° C. using dry hydrogen, corresponding to 9.1% of hydrogen atoms, and with flow rates similar to those used previously with normal butane (12). The sole product was found to be methane, in agreement with the earlier study, but the amount of reaction was approximately one-half that reported previously. On the other hand, a single experiment with propane, also using dry hydrogen at 35° C., and with flow rates comparable to those used by Steacie and Parlee (13) gave results which agreed with their data with respect to the products formed and to the hydrogen atom concentrations used, as estimated from the relative amounts of reaction. It seems possible, therefore, that the hydrogen atom concentrations actually present during the normal butane study were considerably higher than reported. While an error in the atom concentration, even several-fold, would not materially affect the conclusions drawn, it would mean that the data for normal butane should be compared with those for isobutane at the higher atom concentrations. The only difference in the general behaviour of the two compounds, apart from reactivity, apparently then would be the presence, particularly at higher temperatures, of small amounts of propane in the products from isobutane.

Any attempt to formulate a mechanism for the reaction of isobutane with hydrogen atoms must take into account the presence of methane alone in the products at low temperatures, the presence of ethane and small amounts of propane at higher temperatures, and the dependence of the relative amounts of the major products on hydrogen atom concentration.

The Primary Reaction

The possible primary steps are:

(*a*) *Hydrogen abstraction:*

$$i\text{-}C_4H_{10} + H \longrightarrow C_4H_9 + H_2 .$$

This type of reaction has been postulated for hydrogen atom reactions with other hydrocarbons (12, 13, 14). It does not seem possible, on the basis of available information, and in view of the uncertainty in assigning a steric factor, to establish whether this reaction should correspond to removal of a primary, or the tertiary, hydrogen atom of the molecule.

(*b*) *Chain breaking:*

The chain breaking reactions which may be postulated for the primary step are:

$$\begin{aligned} i\text{-}C_4H_{10} + H &\longrightarrow C_3H_8 + CH_3 \\ &\longrightarrow C_3H_7 + CH_4 . \end{aligned}$$

If the first of these occurred, considerable propane should have been present in the products at low temperatures. Since propane was not found in measurable quantities except at 250° C., this reaction may be ruled out as the primary step. By analogy, the second reaction may also be ruled out. Moreover, such reactions are analogous to:

$$C_2H_6 + H \longrightarrow CH_3 + CH_4 ,$$

for which the activation energy has been estimated as approximately 30 kcal. The fact that the chain breaking would occur at a tertiary carbon atom in isobutane probably would not decrease the activation energy appreciably, and any reaction of this type can probably be excluded as the primary step. The abstraction of a hydrogen atom would thus appear to be the primary reaction.

Secondary Reactions

At temperatures between 30° and 140° C. the only product found in appreciable amount was methane. This behaviour is explained most readily by assuming a series of "atomic cracking" reactions subsequent to the primary step, as first suggested by Rice and Teller (10) and elaborated subsequently by Taylor (16). Regardless of whether a primary, or the tertiary, hydrogen atom is abstracted in the primary step, the first of these reactions presumably forms the isopropyl radical:

$$C_4H_9 + H \longrightarrow i\text{-}C_3H_7 + CH_3\,,$$

which may be followed by:

$$i\text{-}C_3H_7 + H \longrightarrow C_2H_5 + CH_3$$
$$C_2H_5 + H \longrightarrow 2CH_3\,.$$

This last reaction was originally suggested to account for the formation of methane in the reaction of hydrogen atoms with ethane (10). The activation energy has been estimated to be about 5 kcal. A similar value is probable for the reaction of the isopropyl radical with hydrogen atoms. The occurrence of such reactions has received considerable experimental (12, 13) and theoretical (6, 10) support.

Reactions of radicals with hydrogen molecules apparently do not occur at the lower temperatures since, with the exception of methyl radicals, the products should be ethane, propane, etc., which were not found in significant amounts below the temperature range 140° to 170° C. This is in agreement with recent investigations which indicate that the reaction of methyl radicals with molecular hydrogen does not have a measurable rate below about 160° C. (9, 17). Radical recombination reactions also appear to play virtually no part in the over-all changes, since these too should give rise to products other than methane at low temperatures. Presumably the concentration of hydrogen atoms was so much greater than that of radicals that the "atomic cracking" reactions occurred almost exclusively. The traces of ethane and propane found at the lower temperatures probably represent the maximum extent to which recombination of radicals occurred.

Above 140° C., or 170° C., depending upon the hydrogen atom concentration, appreciable quantities of ethane appeared in the products. In the higher temperature range reactions of radicals with molecular hydrogen and radical decomposition reactions might be expected to become increasingly prominent.

Reactions between radicals and hydrogen molecules might occur as follows:

$$i\text{-}C_3H_7 + H_2 \longrightarrow C_3H_8 + H$$
$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H$$
$$CH_3 + H_2 \longrightarrow CH_4 + H.$$

The probable radical decomposition reactions would seem to be:

$$C_4H_9 \longrightarrow C_3H_6 + CH_3$$
$$\longrightarrow C_2H_4 + C_2H_5$$
$$i\text{-}C_3H_7 \longrightarrow C_2H_4 + CH_3\,.$$

Any unsaturate formed must have been hydrogenated rapidly, since none was detected in the analyses of the products.

The increase in the ethane : methane ratio observed with increased hydrogen atom concentration at the higher temperatures apparently cannot be explained on the basis of a reaction between hydrogen atoms and propylene. This reaction has been studied by the discharge tube method (2), and found to yield methane, ethane, and propane. Preliminary work indicates, however, that as the hydrogen atom concentration is increased relative to that of propylene the proportion of methane to ethane increases; this is the reverse of the behaviour observed in the isobutane reaction. Similarly, it seems likely that an increased methane : ethane ratio would accompany an increase in the relative hydrogen atom concentration in the corresponding reaction with ethylene. This point is being investigated at the present time.

The increase in the proportion of ethane in the products, with increase in the hydrogen atom concentration at the higher temperatures probably results from an increased production of ethyl radicals, which undergo reaction with hydrogen molecules at these temperatures to form ethane according to (cf. (13)):

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H,$$

or possibly by a ternary collision, as suggested (15) for the corresponding reaction of methyl radical:

$$2C_2H_5 + H_2 \longrightarrow 2C_2H_6 .$$

While the reaction of methyl radicals with hydrogen molecules should also gain in prominence at the higher temperatures, the relative extent to which methyl radicals are produced from ethyl radicals by the action of hydrogen atoms might be expected to be diminished as a result of ethane formation.

The presence of some propane in the reaction of isobutane with hydrogen atoms, in contrast with its absence in the normal butane reaction, is explicable if it is accepted that normal butane produces normal propyl, and isobutane produces isopropyl radicals. The absence of propane in the reaction products with normal butane has been explained by assuming that the reaction of propyl radicals with hydrogen molecules occurs at an appreciable rate only at a temperature higher than that at which the radicals are destroyed before they can react (12). The isopropyl radical appears to be slightly more stable than the normal propyl radical (5). Some propane might be produced, therefore, by the reaction of isopropyl radicals with molecular hydrogen at higher temperatures.

References

1. BONHOEFFER, K. F. and HARTECK, P. Photochemie. Leipzig. 1933.
2. DAVIS, S. G., RABINOVITCH, B. S., and WINKLER, C. A. Unpublished results.
3. FARKAS, A. and MELVILLE, H. W. Experimental methods in gas reactions. Macmillan and Company, Ltd., London. 1939.
4. FRANKENBURGER, W. and ZELL, R. Z. physik. Chem. B, 2 : 395-398. 1929.
5. GLAZEBROOK, H. H. and PEARSON, T. G. J. Chem. Soc. 1936 : 1777-1779.
6. GORIN, E., KAUZMANN, W., WALTER, J., and EYRING, H. J. Chem. Phys. 7 : 633-645. 1939.
7. HERZFELD, K. F. Kinetische theorie der wärme. Braunschweig. 1925.
8. MOORE, W. J., JR. and TAYLOR, H. S. J. Chem. Phys. 8 : 396-403. 1940.

9. Morikawa, K., Benedict, W. S., and Taylor, H. S. J. Chem. Phys. 5 : 212-225. 1937.
10. Rice, F. O. and Teller, E. J. Chem. Phys. 6 : 489-496. 1938.
11. Steacie, E. W. R. Can. J. Research, B, 15 (6) : 264-273. 1937.
12. Steacie, E. W. R. and Brown, E. A. J. Chem. Phys. 8 : 734-738. 1940.
13. Steacie, E. W. R. and Parlee, N. A. D. Can. J. Research, B, 17 (12) : 371-384. 1939.
14. Steacie, E. W. R. and Phillips, N. W. F. J. Chem. Phys. 4 : 461-468. 1936.
15. Taylor, H. A. and Burton, M. J. Chem. Phys. 7 : 675-679. 1939.
16. Taylor, H. S. J. Phys. Chem. 42 : 763-772. 1938.
17. Taylor, H. S. and Rosenblum, C. J. Chem. Phys. 6 : 119-123. 1938.
18. Titani, T. Bull. Chem. Soc. Japan, 5 : 98-108. 1930.
19. Trenner, N. R., Morikawa, K., and Taylor, H. S. J. Chem. Phys. 5 : 203-211. 1937.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 20, SEC. B. DECEMBER, 1942 NUMBER 12

THE NATURAL OCCURRENCE OF 3-METHOXY-PYRIDINE[1]

BY RICHARD H. F. MANSKE[2]

Abstract

A volatile base, identified as 3-methoxy-pyridine, has been isolated from *Thermopsis rhombifolia* (Nutt.) Richards and from *Equisetum arvense* L.

The alkaloids of *Thermopsis rhombifolia* (Nutt.) Richards have been under investigation by the author for some time, but owing to the difficulties of crystallization of some of the fractions it is expected that publication will be further delayed.

In the meantime it seems advisable to record the isolation of a small amount of a very volatile base, which has been identified as 3-methoxy-pyridine. It constituted about 3% of the total bases, which in turn were present to the extent of 0.25% in the dried whole plant exclusive of roots. Its positive identification necessitated the synthesis of an authentic specimen because the properties of its derivatives deviated considerably from the recorded values. It was ultimately purified as its picrate (m.p. 139° C.)*, which had not previously been prepared. The base regenerated from the latter was distilled *in vacuo* and from this the double mercurichloride and the platinichloride were prepared. Meyer (4) first prepared 3-methoxy-pyridine by treating 3-hydroxy-pyridine with diazomethane, and he recorded the melting points of the mercurichloride and of the platinichloride as 110° C. and 182° C. respectively. Later, Koenigs, Gerdes, and Sirot (2) prepared 3-methoxy-pyridine by heating 3-bromo-pyridine with sodium methylate in methanol at 150° C. for 48 hr. They recorded that the platinichloride melts at 269° C. and remarked that it is very sparingly soluble.

When the author repeated the latter preparation of 3-methoxy-pyridine, it was found that the product contained a considerable amount of bromine, and no pure picrate could be isolated from it. Ciamician and Dennstedt (1) had already shown that 3-bromo-pyridine could be reduced to pyridine by means of zinc and hydrochloric acid. The mixture of methoxy- and bromo-pyridine was therefore reduced with this reagent and the fraction of the regenerated base that boiled above 150° C. was redistilled *in vacuo*. It was then free of bromine and the picrate prepared from it melted at 139° C. either

---

[1] *Manuscript received September 29, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1094.

[2] *Chemist.*

* *All melting points are corrected.*

alone or in admixture with the specimen of natural origin. The mercurichloride and the platinichloride melted at 120° C. and 194° C. respectively, and no depression was observed in these melting points when the synthetic and natural products were mixed. The high melting point (269° C.) of the platinichloride of 3-methoxy-pyridine recorded by Koenigs and co-workers can now be explained. They prepared their derivative from a product that undoubtedly contained bromine, and it has now been observed that the platinichloride of 3-bromo-pyridine is much less soluble than that of 3-methoxy-pyridine. A specimen of the former prepared from pure 3-bromo-pyridine melted in its water of crystallization at about 200° C. It then resolidified at 210 to 220° C. and finally melted at 268 to 269° C. Ciamician and Dennstedt (1) had already prepared 3-bromo-pyridine platinichloride and showed that it has two molecules of water of crystallization. It is obvious therefore that Koenigs, Gerdes, and Sirot actually had in their possession the platinichloride of 3-bromo-pyridine instead of that of 3-methoxy-pyridine in spite of the almost perfect platinum analysis that they recorded for the latter.

In the course of an examination of the bases of *Equisetum arvense* L. the author in collaboration with L. Marion (3) obtained a few milligrams of a very volatile base (more volatile than nicotine, from which it was separated by fractional distillation) that yielded a picrate melting at 135° C. A single analysis indicated that the picrate was that of a base, C_6H_7ON. The crude picrate from *T. rhombifolia* also melted at 135 to 136° C. and a mixture of the two substances melted at this temperature. When the *Equisetum* base picrate was recrystallized once from methanol it melted at 137 to 138° C. and this when admixed with pure 3-methoxy-pyridine picrate also melted at 137 to 138° C. There is therefore no question but that at least one species of *Equisetum* also contains this, perhaps the simplest of natural bases.

Experimental

Isolation of 3-Methoxy-pyridine

The mixture of total ether soluble bases from *T. rhombifolia* was slowly heated to 150° C. *in vacuo* (1 mm.), and the distillate, which was collected in a cooled receiver, was redistilled. The fraction boiling at 40 to 60° C. (1 mm.) was dissolved in hot methanol and treated with twice its weight of picric acid also dissolved in hot methanol. The picrate, which crystallized almost at once (m.p. 135 to 136° C.), was recrystallized twice more from hot methanol. It was then obtained in large stout prisms that melt sharply at 139° C., and further recrystallization failed to alter this value. Found: C, 42.81, 42.53; H, 2.96, 3.07; N, 16.41%. Calc. for $C_{12}H_{10}O_8N_4$; C, 42.60; H, 2.96; N, 16.57%.

The free base was obtained by suspending the picrate in an excess of aqueous sodium hydroxide and shaking with ether. The ether solution was washed with a little water, dried over sodium hydroxide, and the solvent distilled off. The residue was distilled *in vacuo* and boiled at 40° C. (1 mm.). The colourless base thus obtained had an odour much like that of pyridine and showed a slight blue fluorescence. Found: C, 66.09, 66.02; H, 6.39, 6.40; OMe, 27.20%. Calc. for C_6H_7ON: C, 66.05; H, 6.42; OMe, 28.18%.

The *mercurichloride* was prepared by adding mercuric chloride in methanol to a methanolic solution of the base containing an excess of hydrochloric acid. Some of the methanol was evaporated and hot water added. The double salt then crystallized in large brilliant prisms that melted at 120° C. Recrystallization from hot water, in which it is moderately soluble, did not alter this value.

The *platinichloride* crystallized in golden plates when a methanolic solution of platinic chloride was added to a solution of the base in methanolic hydrochloric acid. It melted sharply at 194° C.

The *aurichloride* crystallized slowly from water in pale yellow fragile needles that melted at 176° C.

Synthesis of 3-Methoxy-pyridine

A mixture of 3-bromo-pyridine (28 gm.) and sodium methylate (4.6 gm. of sodium in 40 cc. of methanol) was heated in a steel autoclave at 150 to 160° C. for 48 hr. Most of the methanol was evaporated from the mixture, which was then extracted with ether. The residue from the ether extract was twice distilled *in vacuo* (b.p. about 50° C. (1 mm.)). It contained large quantities of halogen and a picrate prepared in methanol melted indefinitely at 115 to 130° C.

The total base was then dissolved in dilute hydrochloric acid and gently boiled for four to five hours with an excess of granulated zinc. The base was recovered by adding an excess of aqueous sodium hydroxide to the filtered solution and extracting with ether. The residue from the ether extract was distilled at atmospheric pressure until the temperature of the vapour rose to 150° C. The remainder was then distilled and redistilled *in vacuo*. There was thus obtained 6 gm. of water-white 3-methoxy-pyridine, which gave a negative test for halogen.

The picrate melted at 137 to 138° C. and when recrystallized from hot methanol it melted sharply at 139° C. either alone or in admixture with a specimen of the picrate obtained from *T. rhombifolia*.

The mercuri-chloride and the platinichloride were prepared as above described. Their melting points were the same as those of the corresponding derivatives of natural origin, and the appropriate mixtures showed no depression in melting points.

References

1. Ciamician, G. L. and Dennstedt, M. Ber. 15 : 1172-1181. 1882.
2. Koenigs, E., Gerdes, H. C., and Sirot, A. Ber. 61(5) : 1022-1030. 1928.
3. Manske, R. H. F. and Marion, L. Can. J. Research, B, 20(5) : 87-92. 1942.
4. Meyer, H. Monatsh. 26 : 1311-1329. 1905.

TASTE DIFFERENCES IN COMPOUNDS HAVING THE NCS LINKAGE[1]

BY C. Y. HOPKINS[2]

Abstract

A group of compounds consisting of thion-thiazolidines, thion-oxazolidines, and a thion-thiazoline were found to be tasteless to some persons and very bitter to others. The three oxo-thiazolines that were examined did not exhibit this difference, being tasteless to all the subjects. A number of these compounds have been prepared for the first time, and their synthesis is described.

Taste tests were conducted on other sulphur compounds and it is concluded that the "dual taste reaction" accompanies the $-\mathrm{NH}-\underset{|}{\mathrm{C}}=\mathrm{S}$ grouping.

Introduction

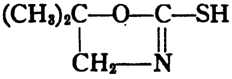
During a study of the bitter principle of the seed of *Conringia orientalis* (3), the author isolated the substance 2-mercapto-5,5-dimethyl-oxazoline and found it to be tasteless. Shortly afterwards, Mr. D. C. Caplan, working in the same laboratory, was bottling a small quantity of the substance and remarked that it had an intensely bitter taste.

It was apparent that this compound has the peculiar characteristic found by Fox in phenylthiourea (1), viz., that it is tasteless to some persons and very bitter to others. The fact was confirmed by conducting taste tests with a number of individuals.

Although Fox examined a large number of thiourea derivatives and found that nearly all had the dual taste reaction, the present instance is the first in which it has been found in a nitrogen ring compound. Accordingly, taste tests were carried out with several compounds prepared during the previous investigation and on others of similar constitution.

Nomenclature

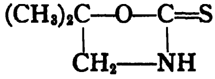
2-Mercapto-5,5-dimethyl-oxazoline is very probably tautomeric and so may exist in the mercapto or thion form. The thion formula (II) is preferred.



$$\begin{array}{lcl}(\mathrm{CH_3})_2\mathrm{C}-\mathrm{O}- & \mathrm{C}-\mathrm{SH} \\ \quad\;\; | & \| \\ \quad\;\; \mathrm{CH_2}- & \mathrm{N}\end{array}$$

I

2-Mercapto-5,5-dimethyl-oxazoline



$$\begin{array}{lcl}(\mathrm{CH_3})_2\mathrm{C}-\mathrm{O}- & \mathrm{C}=\mathrm{S} \\ \quad\;\; | & | \\ \quad\;\; \mathrm{CH_2}- & \mathrm{NH}\end{array}$$

II

2-Thion-5,5-dimethyl-oxazolidine

---

[1] *Manuscript received August 13, 1942.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1092.

Presented before Section III of the Royal Society of Canada, May 24, 1939.

[2] *Chemist.*

Taste Tests with Thiazo and Oxazo Compounds

Table I shows the results of taste tests by the author (C.Y.H.) and by Mr. Caplan (D.C.C.) with a number of cyclic oxygen and sulphur compounds whose taste has not hitherto been reported.

Tests were ordinarily made by tasting the crystals of each substance. The compounds in Table I have a slight solubility in water, being similar to phenylthiourea in this respect. Some trials were made with dilute solutions but no advantage was found in using this method.

Substances having the dual taste reaction are classed as positive, while those that taste the same to all individuals are referred to as negative.

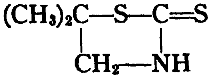
TABLE I

TASTE TESTS WITH THIAZO AND OXAZO COMPOUNDS

Substance	Taste sensation		Dual taste reaction
	(C.Y.H.)	(D.C.C.)	
2-Thion-5,5-dimethyl-oxazolidine II	Tasteless	Very bitter	+
2-Thion-5,5-dimethyl-thiazolidine	Tasteless	Very bitter	+
2-Thion-5-methyl-oxazolidine	Tasteless	Very bitter	+
2–Thion-5-methyl-thiazolidine	Tasteless	Very bitter	+
2-Thion-thiazolidine	Tasteless	Very bitter	+
2-Oxo-4,5-dimethyl-thiazoline	Tasteless	Tasteless	−
2-Thion-4,5-dimethyl-thiazoline	Tasteless	Very bitter	+
2-Oxo-4-methyl-thiazoline	Tasteless	Tasteless	−
2-Oxo-4-methyl-5-bromo-thiazoline	Tasteless	Tasteless	−
2-Thion-4,4-dimethyl-oxazolidine	Tasteless	Very bitter	+

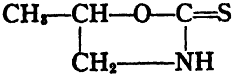
The taste tests were confirmed by repeating the tests with a group of individuals, some of whom were tasters and some non-tasters, as determined by their reaction to phenylthiourea. Upon tasting the substances listed in Table I, the "tasters" experienced the same sensations as did Mr. Caplan, while the non-tasters found all the materials to be tasteless.

Considering substance II, it was found that replacement of the oxygen in the ring by sulphur did not destroy the dual taste reaction:

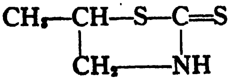


2-Thion-5,5-dimethyl-thiazolidine

The corresponding pair of compounds with one methyl group had the same characteristic:

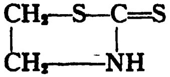


2-Thion-5-methyl-oxazolidine



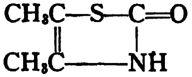
2-Thion-5-methyl-thiazolidine

Elimination of the substituent methyl group had likewise no effect on the peculiar taste reaction:



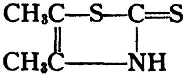
2-Thion-thiazolidine

However, on replacing the thion sulphur by oxygen, the bitterness disappeared and this substance was tasteless to all the subjects:



2-Oxo-4,5-dimethyl-thiazoline

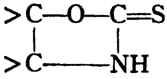
The corresponding thion-thiazoline was bitter to the so-called tasters and tasteless to the non-tasters:

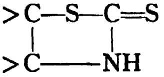


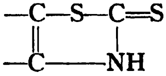
2-Thion-4,5-dimethyl-thiazoline

2-Oxo-4-methyl-thiazoline was found to be tasteless to all the subjects.

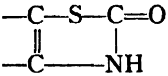
Summarizing the data, it is observed that the following groupings, with various substituents, gave the dual taste reaction,







while the oxo-thiazoline derivatives did not,



The grouping —NH—$\underset{|}{\text{C}}$=S appears to be connected with the unusual taste characteristic and the arrangement —NH—$\underset{\|}{\text{C}}$—S— apparently does not give this effect.

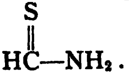
Taste Tests with Various Sulphur Compounds

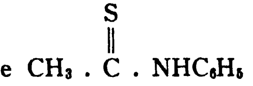
Further tests were carried out with common substances as shown in Table II.

TABLE II

TASTE TESTS WITH OTHER —N—C=S COMPOUNDS

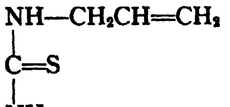
Substance	Taste sensation (C.Y.H.)	Taste sensation (D.C.C.)	Dual taste reaction
Phenylthiourea	Tasteless	Very bitter	+
Thioacetamide	Almost tasteless	Very bitter	+
Thioacetanilide	Tasteless	Very bitter	+
Isodithiocyanic acid	Tasteless	Very bitter	+
Allylthiourea	Momentary faint bitterness	Very bitter and persistent	+
Thiobarbituric acid	Faint taste	Faint taste, not bitter	—

The simplest substance having the NHCS group is thioformamide,  $H\overset{\overset{S}{\|}}{C}-NH_2$. It has been described by Willstätter as very bitter. This substance was not readily available. Thioacetamide, however, was found to be very bitter to the tasters and almost tasteless to the non-tasters. Thioacetamide is very soluble in water and it is evident, therefore, that the bitter taste is not dependent upon the degree of solubility, since it was virtually tasteless to certain persons. Although thioacetamide is a very common material, this taste difference has not hitherto been observed. It is remarkable also that Cohn, author of the exhaustive work on taste, "Die Organischen Geschmackstoffe", failed to realize that the same substance might taste differently to different persons. He actually reported one or two such cases but stated that one observer must have been mistaken.

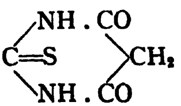
In thioacetanilide  $CH_3 \,.\, \overset{\overset{S}{\|}}{C} \,.\, NHC_6H_5$ one of the amino hydrogens is substituted but the taste difference remains. Fox (1) found that if both hydrogens are substituted, as in tetramethyl thiourea, the taste difference disappears.

On the basis of these observations, it is concluded that the dual taste reaction accompanies the grouping $-NH-\underset{|}{C}=S$. Some 20 thiourea derivatives prepared by Fox and containing this grouping were shown to taste differently to different persons and 11 of the substances described above exhibited the same characteristic. The reaction of tasters to isodithiocyanic acid, $\underbrace{NH \,.\, CS \,.\, NH \,.\, CS}$, confirms this theory.

All compounds having the $-NH-\underset{|}{C}=S$ group do not necessarily have the dual taste reaction. Various substituents may influence the taste so as to overshadow the effect of the NHCS group. Thus thiourea itself is not bitter but sour to all persons (1). Allylthiourea has a momentary bitterness even to the so-called non-tasters (Table II). The unsaturation appears to intensify the bitterness, as shown also in crotylthiourea (1). On the other hand thiobarbituric acid is exceptional in that it has no bitter taste to persons of either group. It is possible that the CO groups overcome the influence of the CS group towards bitterness.



Allylthiourea



Thiobarbituric acid

Preparation of Compounds Listed in Table I.

2-Thion-5,5-dimethyl-oxazolidine. (3).

2-Thion-5,5-dimethyl-thiazolidine. A sample of this material was kindly supplied by Dr. H. A. Bruson.

2-Thion-5-methyl-oxazolidine. Twenty-five grams of 1-aminopropanol-2 and 38 gm. of carbon disulphide were mixed gradually with cooling. A solution of 28 gm. of potassium hydroxide in 20 cc. of water and 150 cc. of ethanol was added and the mixture was refluxed for 2½ hr. After distilling off most of the alcohol, water was added, and the solution was extracted with chloroform. The material obtained from the extract was recrystallized several times from benzene. When pure it melted at 72 to 73°.* Found: C, 41.03; H, 6.17; S, 27.43%. Calc. for C_4H_7ONS: C, 41.03; H, 6.03; S, 27.38%. It is soluble in alcohol, ether and benzene, moderately soluble in water, and insoluble in hexane.

2-Thion-5-methyl-thiazolidine. Gabriel (2, p. 814) prepared this substance from β-bromopropylamine and carbon disulphide and gave its melting point as 88 to 89° (uncorrected). The material obtained in the present work melted at 92 to 93° uncorrected (93 to 94° corrected). Found: C, 36.21, 36.12; H, 5.23, 5.15; N, 10.21, 10.32%. Calc. for $C_4H_7NS_2$: C, 36.07; H, 5.30; N, 10.52%. The procedure was as follows: twenty-five grams of 1-aminopropanol-2 was mixed while cooling with 50 gm. of carbon disulphide. A solution of 28 gm. of potassium hydroxide in 20 cc. of water and 150 cc. of ethanol was added and the mixture was refluxed for six hours. The alcohol was distilled off and the residue was acidified with 1 : 1 sulphuric acid. The crystals (largely inorganic) were filtered off and leached with hot benzene. The benzene solution was concentrated and cooled, whereupon the product crystallized out. The yield was poor.

2-Thion-thiazolidine. This substance was prepared from 1-aminoethanol-2 and carbon disulphide according to the method of Knorr and Rössler (5).

2-Oxo-4,5-dimethyl-thiazoline. A mixture of 5 gm. of 3-chlorobutanone-2, 6 gm. of potassium thiocyanate, 1.5 gm. of sodium bicarbonate and 75 cc. of water was allowed to stand for three days. The solid product was filtered off and recrystallized from benzene. It melted at 149 to 150°. Found: C, 46.32; H, 5.65; N, 10.87; S, 24.72%. Calc. for C_5H_7ONS: C, 46.49; H, 5.46; N, 10.84; S, 24.82%. It is soluble in alcohol, moderately soluble in ether, chloroform and benzene, slightly soluble in water, and insoluble in hexane.

2-Thion-4,5-dimethyl-thiazoline. Fifteen grams of 3-chlorobutanone-2 and 12 gm. of ammonium dithiocarbamate were mixed in 100 cc. of alcohol. Considerable heat was evolved. The mixture was allowed to stand 12 hr. and was then refluxed for one hour. Water was added, most of the alcohol was distilled off, and the solution was cooled. The crystals that formed on standing were recrystallized from benzene; the product melted at 166 to 168°.

---

* *Melting points are corrected.*

Found: N, 9.54%. Calc. for $C_6H_7NS_2$: N, 9.66%. It is soluble in alcohol and ether, moderately soluble in benzene, difficultly soluble in water, and insoluble in hexane.

2-Oxo-4-methyl-thiazoline (oxymethylthiazole). This substance was prepared from choroacetone and potassium thiocyanate by the method of Tcherniac (7). It is not necessary to let the reaction proceed for 10 days, however, since the product may be extracted after two days with only a slight sacrifice in yield. Further time is saved by extracting with chloroform instead of ether, since the material is more soluble in the former. Recrystallization is best done in benzene with cooling to 0° C.

When the reaction was carried out in alcohol instead of water, a substance was obtained that was insoluble in benzene. After recrystallization from alcohol it melted at 193°. It was not investigated further.

2-Oxo-4-methyl-5-bromo-thiazoline. This substance was prepared by the method of Ochiai and Nagasawa (6, p. 1471). It crystallizes in silky needles, m.p. 150° C., and is soluble in alcohol and ether, slightly soluble in benzene and chloroform, and insoluble in hexane.

2-Thion-4,4-dimethyl-oxazolidine. Thirty grams of 2-amino-2-methyl-1-propanol and 38 gm. of carbon disulphide were mixed gradually with cooling. A solution of 28 gm. of potassium hydroxide in 20 cc. of water and 150 cc. of ethanol was added and the mixture was refluxed for 2½ hours. After distilling off most of the alcohol, 150 cc. of water was added and the solution was extracted with chloroform. The material obtained from the extract was recrystallized from benzene. When pure it melted at 123 to 125° C. Found: N, 10.80%. Calc. for C_5H_9ONS: N, 10.69%. It is soluble in alcohol, ether, and benzene, moderately soluble in water, and insoluble in hexane.

Acknowledgment

The author is indebted to Mr. A. E. Ledingham for his kindness in performing the analyses.

References

1. Fox, A. L. Proc. Natl. Acad. Sci. U. S. 18(1) : 115-120. 1932.
2. Gabriel, S. and Ohle, H. Ber. 50 : 804-818. 1917.
3. Hopkins, C. Y. Can. J. Research, B, 16(9) : 341-344. 1938.
4. Julian, P. L. and Sturgis, B. M. J. Am. Chem. Soc. 57(6) : 1126-1128. 1935.
5. Knorr, L. and Rössler, P. Ber. 36 : 1278-1283. 1903.
6. Ochiai, E. and Nagasawa, F. Ber. 72(7) : 1470-1476. 1939.
7. Tcherniac, J. J. Chem. Soc. 115 : 1071-1090. 1919.

SOME SOURCES OF VITAMIN C IN ALBERTA[1]

BY HILDA K. WAAGEN[2] AND L. B. PETT[3]

Abstract

Some fruits and vegetables grown in Alberta were investigated as sources of Vitamin C, and the loss occasioned by cooking was determined. Losses due to oxidation during cooking were compared with those due to extraction by the cooking water. Both cause considerable loss of vitamin C from the vegetable pulp; it would therefore be more economical always to use the juice from the vegetables. The vitamin C content of potatoes varies with the season, the peak being reached in September and just before the first frost occurs, and being followed by a steady decrease during storage.

Introduction

Two main factors determine the quantity of vitamin C in the diet, namely; the food, or the source, and the method of preparation for consumption. These factors are of equal importance and their value depends on several different conditions. Thus, as is generally known, the vitamin C content of vegetables and fruits varies with the season, variety, soil conditions, and locality. Similarly the mode of preparation is dependent on the facilities, the type of cooking, and the cook's knowledge regarding means of preservation of the vitamin C.

Extensive surveys have been carried out in many countries to ascertain the best and cheapest sources of vitamin C (2–5, 7, 8, 12). Since the ascorbic acid contents of vegetables and fruits vary under different conditions, the values obtained in other countries cannot always be accepted as criteria of the values for Canadian products. It is thus desirable that surveys of Canadian vegetables and fruits should be carried out.

In this paper an indication is given of the vitamin C content to be expected in certain vegetables and fruits. The content of the vitamin in a few samples of numerous different fruits and vegetables, rather than in many samples of two or three, was determined. The samples were tested before and after cooking, to determine the loss of vitamin C during food preparation. Also included in the paper are the values obtained with foods tested during the year's survey of the Athabasca Hall dietary (11).

Experimental

A survey of the vitamin C content of locally grown vegetables and fruits was carried out. All vegetables were tested as soon after harvesting as possible, usually on the same day. If any had to be left over, they were

---

[1] *Manuscript received in original form August 3, 1942, and, as revised, September 1, 1942.*
Contribution from the Department of Biochemistry of the University of Alberta, Edmonton, Alta., with financial assistance derived from a grant to Prof. G. Hunter from the Associate Committee on Medical Research of the National Research Council of Canada. This work was included in a thesis for the degree of Master of Science in the University of Alberta.

[2] *Formerly Research Assistant, 1939–41.*

[3] *Director of Nutrition Services, Department of Pensions and National Health, Ottawa. At the time, Lecturer in Biochemistry, University of Alberta.*

put in the icebox at 5° C. until ready for use. The large vegetables, such as potatoes, turnips, carrots, etc., were cut into two equal parts, one of which was tested in the raw condition for vitamin C, and the other was first cooked, then tested. The vegetables were boiled in water in sufficient quantity just to cover them until done, overcooking being avoided.

The method of preparation of the tissue extract and the titration were the same as in previous work (11).

During the survey of the Athabasca Hall dietary, the vitamin C contents of many different foods were determined. The list is included in this paper as a supplement to the values obtained on locally grown vegetables. Description of the method of the survey was given in a preceding paper (11).

Results

Table I was compiled from results obtained in determinations carried out on vegetables and fruits grown in the University of Alberta gardens.

The loss of vitamin C during cooking varies greatly; it is considerable in some vegetables, small in others, and the occasional vegetable shows an apparent increase. The percentage loss is less in fruits owing to their acidity (1). In the cooking of leafy vegetables such as kale, broccoli, and beet tops there is a tendency for the vitamin C to be largely destroyed. There is also high loss in celery and onions; the reason for this is not apparent.

The vitamin C content varies with the variety of the vegetable and with the individual plants of the same variety. The average value and the range give the best indication of the content. Of the raw vegetables, parsley was found to have the highest vitamin C value; rhubarb, the lowest. Of the cooked vegetables and fruits, strawberries have the highest vitamin C content, with black currants a close second. Broccoli, kale, Brussel sprouts, and asparagus tips are good sources of the vitamin. Since potatoes are so universally consumed during the winter and summer, and in large amounts, they are good sources.

It is noted that the vitamin C content of asparagus tips is double that of the stalks; this agrees with the results obtained by Olliver (7). Wheeler *et al.* (13) note that the vitamin C content of the outer leaves of the lettuce is slightly higher than that of the inner. This is in agreement with our values for lettuce.

There has been much controversy concerning the cause of the apparent increase of vitamin C content on heating some vegetables. Reedman and McHenry (9) maintain that the vitamin is present as a protein conjugate, which is broken down on heating to give free ascorbic acid. Olliver (7) suggests that there may be incomplete extraction from the raw vegetables, especially woody ones, which are difficult to grind. On cooking, the tissues are softened, and the extraction of vitamin C is more complete, with resultant higher estimates. Van Eekelen (10) suggests that the increase after cooking is due to the destruction of the ascorbic acid oxidase. The latest suggestion made by Mack and Tressler (6) is that the apparent increase is caused by the decomposition of dehydro ascorbic acid into physiologically inactive but strongly reducing products. The question is far from answered. But as

TABLE I

PERCENTAGE LOSS OF VITAMIN C IN COOKING. VITAMIN C EXPRESSED IN MG. PER 100 GM. WET WEIGHT

Vegetable or fruit	Variety	No. of samples	Average no. mg. Vitamin C, and range		Average loss, %
			Raw	Cooked	
Asparagus—tips	Mary Washington	4	52 (35 – 69)	32 (18 – 51)	38.0 (26.5 – 65.8)
—stalks		4	22 (11 – 32)	16 (10 – 24)	24.3 (20.6 – 57.2)
Beans	Yellow Wax	1	29	24	18
	Green String	1	37	22	39
Beets—tops	Detroit Dark Red	1	44	19	56
	Crosby's Egyptian	1	40	19	53
	Lutz's Greenleaf	1	45	20	55
—roots	Detroit Dark Red	1	14	6.1	57
	Crosby's Egyptian	1	13	15	
	Lutz's Greenleaf	1	4.7	6.6	
Broccoli	Sprouting	3	94 (83 – 102)	30 (28 – 32)	
Brussels Sprouts		2	81 (Both)	38 (30 – 46)	
Cabbage	Late Green	2	30 (29 – 31)	20 (Both)	
Carrots	Red Cored Chantenay	1	5.4	2.5	
	Streamliner	2	14 (12 – 17)	7 (4 – 10)	
Celery	White	2	11 (10 – 11)	3.1 (2.3 – 3.8)	70.5
	Pink	1	10	2.4	76.0
Cherry	Brooks Sand Cherries	1	10	8.6	16.3
Cherry plum	Sapa	1	10	11	9.3 inc.
	Tom Thumb	1	6.5	9.3	43.2 inc.
Corn		2	8.9 (8.5 – 9.3)	5.8 (4.7 – 7.0)	34.8 (17.9 – 49.6)
Chives		1	36	—	—
Crabapples	Adam (early)	1	6.2	4.1	33.8
	Protosh (late)	1	9.7	10.2	5.8 inc.
Cress		1	35	—	—
Currants	Red	1	27.0	26	3.6
	Black	1	88	62	29.7

TABLE I—*Concluded*

PERCENTAGE LOSS OF VITAMIN C IN COOKING. VITAMIN C EXPRESSED IN MG. PER 100 GM. WET WEIGHT—*Concluded*

Vegetable or fruit	Variety	No. of samples	Average no. mg. vitamin C, and range		Average loss, %
			Raw	Cooked	
Kale		1	77	27	64.5
Marrow	Vegetable Marrow	1	9.6	6.1	36.7
Onion	Welsh Winter	1	15	2.9	81.0
Parsley	Evergreen	1	135	—	—
Peas		2	11 (Both)	17 (Both)	53.6 inc. (53.3 – 54.7)
Plums	Selected Seedling	1	8.3	9.8	18.0 inc.
	Mammoth	1	3.7	2.8	23.9
Potatoes	Netted Gem	4	23 (22 – 24)	18 (17 – 20)	18.5 (11.0 – 25.0)
Radishes	French Breakfast	6	14 (10 – 19)	—	—
Raspberries		1	23	16	27.8
Rhubarb	Macdonald Red	3	1.4 (0.6 – 2.3)	0.4 (0.3 – 0.6)	71.4 (27.8 – 87.9)
Squash	Scallop	1	17	12	29.8
Strawberries	B.C.	1	64	63	1.6
Tomatoes		3	12 (8.4 – 14)	—	—
Turnips	White Milan	2	17 (13 – 21)	6.7 (6.6 – 6.8)	61.5 (50.9 – 68.0)
	White	2	18 (17 – 20)	8.6 (8.6 – 8.6)	53.0 (48.5 – 56.1)
Onions					
bulb		14	21 (8.5 – 39)		
green shoot		14	48 (20 – 97)		
Head lettuce					
Outer leaf		4	11 (5.7 – 22)		
Inner		4	7.7 (1.9 – 16)		
Heart		4	5.4 (0.6 – 12)		

different investigators do not always find the same vegetables showing an increase after heating, it occurs to us that this phenomenon may be manifested by different vegetables in different localities and that it may depend on factors as yet unsuspected.

The vitamin C content of the vegetables and fruits listed was also calculated on a dry weight basis. These are of little practical importance, for it is difficult to visualize our normal consumption of vitamin C in terms of dry weight figures.

Comparison of Cooking Losses due to Oxidation and due to Solution

Tables II and III show a comparison of percentage losses by heat or oxidation, and by solution in the cooking water. Those vegetables showing a loss are listed in Table II, and those showing an apparent gain are listed in Table III.

TABLE II

VEGETABLES AND FRUITS SHOWING LOSS OF VITAMIN C AFTER COOKING. COMPARISON OF LOSSES DUE TO OXIDATION AND DUE TO SOLUTION IN BOILING WATER

Vegetable or fruit	Lost in the boiling water, %	Loss due to oxidation, %	Total loss from pulp, %
Asparagus—tips	33.7	32.1	65.8
—stalks	22.1	35.1	57.2
Beans—string	18.9	20.4	39.3
Black currants	14.5	15.2	29.7
Beet tops	9.8	43.1	52.9
	9.6	45.7	55.3
	5.9	50.7	56.6
Carrots	4.9	57.7	62.6
	2.1	37.6	39.7
Celery—white			
heart	4.4	74.5	78.9
stalk	4.8	56.8	61.6
—pink	1.4	74.6	76.0
Corn	10.4	7.5	17.9
	7.3	42.2	49.5
Crabapples—Adam	7.6	26.1	33.7
Broccoli	26.1	43.1	69.2
	43.4	23.5	66.9
	40.3	28.7	69.0
Brussels sprouts	34.3	9.0	43.3
	41.4	21.1	62.5
Potatoes	14.1	8.0	22.1
	23.0	2.0	25.0
Vegetable marrow	22.3	14.4	36.7

TABLE III

VEGETABLES SHOWING APPARENT INCREASE IN VITAMIN C CONTENT AFTER COOKING

Vegetable or fruit	Mg. vitamin C/100 gm. wet wt.		Mg. vitamin C in water from 100 gm. cooked vegetables	Apparent increase vitamin C in cooked vegetables plus water, %
	Raw	Cooked		
Beans—Wax	29	24	9.1	14
Cabbage	31	20	12	3
	29	20	15	21
Plums—Mammoth	3.7	2.8	1	3
Potatoes	22	19	4.4	6
	24	20	5.9	8
Raspberries	23	16	11	17
Sand cherries	10	8.6	10	86
Scallop squash	17	12	5.1	0.6
Turnips—White				
centre	20	8.6	18	33
outside	17	8.6	21	74
Cherry plum				
Sapa	10	11	14	150
Tom Thumb	6.5	9.3	11	212
Crabapples—Protosh	9.7	10	0.3	6
Peas	11	17	7.3	121
	11	17	5.0	100
Plums—Selected Seedling	8.3	9.8	3.1	56

In Table II, in the first group of three vegetables the loss of vitamin C is about equally due to oxidation and to solution in the cooking water. The results obtained with the second group show oxidation to be the predominating factor in destruction of the vitamin. In the last group, the greater loss occurs through extraction of the vitamin by the cooking water, though the first sample of broccoli is an exception to this. Olliver (8) maintains that the disappearance of vitamin C occurs chiefly by solution in the water, the actual loss depending on the extent of cooking and the amount of water used. These figures indicate that considerable waste can occur through the procedure of discarding the water from vegetables (this is not done with fruits), but whether that or oxidation is the greater factor in the loss of the vitamin seems to depend on which vegetable is considered. It would indeed be more economical to use the water in which the vegetables are cooked.

In Table III the first eight vegetables and fruits listed show increase in content only when the values for the pulp plus the water are taken together. The last four show an increase in the vitamin C content of the cooked vegetable or fruit over that of the raw without including the vitamin C contained in the juice. The juice of fruits is used, so no loss is entailed. The cooking water from turnips and cabbages contains a large proportion of the available vitamin C, as does also that from peas. As noted before, this apparent increase may be due to one of several reasons. These factors may also be active during the cooking of the vegetables listed in Table II. If this be so, oxidation must be playing a still larger part in the destruction of vitamin C than is indicated by the figures.

TABLE IV

VITAMIN C CONTENT OF VEGETABLES AND FRUITS TESTED OVER THE PERIOD OF 13 MONTHS. ARRANGED IN ORDER OF DECREASING AVERAGE VITAMIN CONTENT

Food	Preparation	No. of samples	Range	Mg. ascorbic acid per 100 gm. wet weight. Average
Strawberries	Raw	4	77 – 93	84
Grapefruit	Raw	19	37 – 109[*]	68[*]
Oranges	Raw	65	16 – 61[†]	36[†]
Cauliflower	Steamed	3	24 – 27	26
Cabbage	Raw	9	13 – 32	22
Tomatoes	Raw	33	5 – 29	18
Tomatoes	Canned	6	10 – 25	17
Cabbage	Steamed	6	8 – 28	14
Turnips	Steamed	6	6 – 21	13
Raspberries	Raw	4	8 – 17	12
Parsnips	Steamed	7	4 – 14	8
Bananas	Raw	21	3 – 14	8
Cherries	Raw	4	4 – 12	8
Potatoes	Steamed	130	0 – 35	7
Peaches	Raw	8	2 – 18[‡]	6[‡]
Beets	Steamed	5	3 – 13	6
Cucumbers	Raw	2	5 – 6	6
Pineapple	Canned	7	2 – 10	6
Cherries	Canned	2	4 – 5	5
Beets	Pickled	4	2 – 11	4
Peas	Canned	11	2 – 9	4
Lettuce	Raw	5	2 – 7	4
Rhubarb	Stewed	3	2 – 4	4
Apricots	Canned	7	2 – 5	3
Pears	Canned	10	0 – 10	3
Celery	Raw	4	2 – 4	3
Carrots	Steamed	23	1 – 7	3
Peaches	Canned	8	0 – 4	2
Corn	Canned	12	0 – 6	2
Grapes	Raw	3	1 – 5	2
Beans (string)	Canned	9	0 – 4	2
Apples	Raw	25	1 – 4[§]	2[§]
Celery	Steamed	6	1 – 2	1
Plums	Stewed	4	All	1

Vitamin C is expressed in milligrams per fruit, not per 100 gm., in the cases of grapefruit, oranges, peaches, and apples.

[*] *The average volume of juice in a grapefruit is 160 cc., or 42 mg. ascorbic acid per 100 cc. juice (average).*

[†] *The average volume of juice in an orange is 75 cc., or 48 mg. ascorbic acid per 100 cc. juice (average).*

[‡] *Av. wt. of peaches tested = 110 gm., or 5.5 mg. ascorbic acid per 100 gm. peach (average).*

[§] *Av. wt. of apples tested = 150 gm., or 1.7 mg. ascorbic acid per 100 gm. apple (average).*

Dry weight figures are also available.

Vitamin C Content of Vegetables and Fruits Tested During Athabasca Hall Survey

Table IV lists the values obtained with fruits and vegetables included in the Athabasca Hall dietary throughout 13 months—November, 1939, to November, 1940, inclusive. This table also indicates available sources of vitamin C in Alberta other than local ones (see also Table I).

As shown, fresh strawberries contain the largest amount of vitamin C, but they are available only during the summer months; thus they are not a good year round source. The consumption of oranges and grapefruit is an excellent means of obtaining vitamin C both winter and summer, and, as shown in a previous paper (11), they should certainly be included in the winter diet. Cauliflower, cabbage, turnips, and parsnips are good sources and are available in this country throughout winter and summer. Potatoes form a solid basis for vitamin C nutrition, as they are used regularly in the diet and in large proportion, especially by the poorer classes.

Seasonal Variation of Vitamin C Content of Vegetables

The vitamin C content of potatoes shows a definite seasonal variation, with the values increasing to a peak in September (Table V) or when the potatoes are mature. In Table VI also the highest value is that obtained in September, just before the first frost occurs; the content then drops steadily until at the end of February it is about one-third of the highest value. After September, any further loss is due to storage.

TABLE V

SEASONAL VARIATION OF THE VITAMIN C CONTENT OF SOME FOODS TESTED DURING ATHABASCA HALL SURVEY

Food	Vitamin C												
	Nov.	Dec.	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.
Potatoes (steamed)*	4.3	4.6	2.4	3.3	2.9	1.7	6.1	5.3	7.8	16.0	17.0	16	9.2
Orange†	33	32	50	47	33	28	40	42	31	32	32	43	29
Grapefruit†	56	98	96	82	66	85	50	57	59	54	—	—	43

* *Vitamin C expressed in mg. per 100 gm.*

† *Vitamin C expressed in mg. per fruit.*

After the first frost, the decline in content is first rapid, amounting to 51% in the first month and a half, then a further loss of 20% by the end of 5½ months. The vitamin C content of tomatoes and carrots also exhibits a similar seasonal rise and decline.

In grapefruit and oranges, the content shows a monthly variation, which is dependent on many factors, such as gas ripening, transportation, and variable lengths of storage.

TABLE VI

SEASONAL VARIATION OF VITAMIN C CONTENT OF RAW POTATOES

Dates of samplings	Condition	Average vitamin C content	
		Mg./100 gm. wet wt.	Mg./100 gm. dry wt.
Aug. 23, 1940	Flowering plant	18.4	64.5
Aug. 28 and 30	Not flowering	20.8	75.4
Sept. 3 and 6	Not flowering	27.9	101.8
Sept. 10 and 13	Frost, Sept. 10	34.6	124.4
Sept. 18 and 20	Frost, Sept. 20	27.4	102.5
Sept. 24 and 27		23.0	82.2
Oct. 1 and 4	Dug up and stored Sept. 30	23.5	93.7
Oct. 8 and 12		21.6	91.4
Oct. 15 and 18		21.2	87.2
Oct. 22 and 25		17.8	71.9
Oct. 29 and Nov. 1	Stored one month	17.0	70.0
Nov. 5 and 8		15.0	54.6
Nov. 12 and 15		13.9	51.3
Nov. 19 and 22		13.3	52.8
Nov. 26 and 29		12.2	47.3
Dec. 3 and 6	Stored two months	14.5	53.7
Dec. 10 and 13		12.1	43.6
Dec. 17 and 20		12.5	45.7
Dec. 24		13.8	49.6
Jan. 7 and 10, 1941	Stored three months, six days	10.4	37.2
Jan. 14 and 17		9.0	32.4
Jan. 21 and 24		8.6	31.9
Jan. 28 and 31		11.4	42.8
Feb. 4 and 7	Stored four months	8.0	30.5
Feb. 11 and 14		9.8	36.6
Feb. 21		7.0	30.2
Feb. 25 and 28	Stored five months	9.9	37.2

Comparison of Institutionally and Home-cooked Foods

Where possible, the values obtained during the Athabasca Hall survey were compared with those obtained with locally grown vegetables and fruits. In general the tendency was for the vitamin C content of the foods cooked in an institution to be less than the content of the home-cooked foods.

Comment

This paper presents a general survey of fruits and vegetables that form sources of vitamin C in Alberta diets. Though the problem is local in nature, the results obtained are in all probability applicable to all Western Canada. The importance of the work lies in the furnishing of actual values of the vitamin C content of Alberta grown vegetables and fruits, and the supplementing of these data by those obtained during the investigation of an existing dietary.

Acknowledgments

The writers' indebtedness is expressed to Dr. G. Hunter for his interest; to Dr. J. S. Shoemaker for supplying the fresh vegetables; and to Miss M. Patrick for facilities in the Department of Household Economics.

References

1. BESSEY, O. A. J. Am. Med. Assoc. 111 : 1290-1298. 1938.
2. FENTON, F. and TRESSLER, D. K. Food Research, 3(4) : 409-416. 1938.
3. FENTON, F., TRESSLER, D. K., CAMP, S. C., and KING, C. G. Food Research, 3(4) : 403-408. 1938.
4. JENKINS, R. R., TRESSLER, D. K., and FITZGERALD, G. A. Food Research, 3(1 and 2) : 133-140. 1938.
5. JENKINS, R. R., TRESSLER, D. K., and FITZGERALD, G. A. Ice and Cold Storage, 41 : 100–101. 1938.
6. MACK, G. L. and TRESSLER, D. K. J. Biol. Chem. 118(3) : 735-742. 1937.
7. OLLIVER, M. J. Soc. Chem. Ind. 55 : 153T-163T. 1936.
8. OLLIVER, M. Lancet, 239 : 190-192. 1940.
9. REEDMAN, E. J. and MCHENRY, E. W. Biochem. J. 32 : 85-93. 1938.
10. VAN EEKELEN, M. Nature, 136 : 144-145. 1935.
11. WAAGEN, H. K. and PETT, L. B. Can. J. Research, B, 20(11) : 246-254. 1942.
12. WELLINGTON, M. and TRESSLER, D. K. Food Research, 3(3) : 311-316. 1938.
13. WHEELER, K., TRESSLER, D. K., and KING, C. G. Food Research, 4 : 593-604. 1939.

ENZYME INHIBITION BY DERIVATIVES OF PHENOTHIAZINE

III. CATALASE, CYTOCHROME OXIDASE, AND DEHYDROGENASES[1]

By H. Bruce Collier[2] and Della E. Allen[3]

Abstract

The inhibition of liver catalase and of cytochrome oxidase by leucophenothiazone has been confirmed by manometric methods. Phenothiazine sulphoxide is a powerful catalase inhibitor, its activity being much greater at pH 5.3 than at neutrality.

The succinoxidase activity of beef heart is inhibited by phenothiazone and by thionol. Phenothiazone in its oxidized form acts upon the succinic dehydrogenase, while the leuco form inhibits the cytochrome oxidase.

Phenothiazone is reduced by the yeast lactic dehydrogenase system, and the enzyme activity is markedly decreased. Urease is also partially inhibited, whereas the effect of phenothiazone upon *d*-amino-acid oxidase is almost negligible.

The possible relationship of these findings to the action of phenothiazine upon living organisms is discussed.

Introduction

The first paper in this series (5) described the inhibition of catalase and of cytochrome oxidase by leucophenothiazone, leucothionol, and thionol, all of which are oxidation products of phenothiazine in the animal body (4). This work marked the beginning of a general program designed to explain the anthelmintic activity of the drug phenothiazine. The second paper in the series (7) described the inhibition of serum cholinesterase by phenothiazone and by certain other derivatives of phenothiazine.

The present paper is, in part, an extension of the previous work on catalase and cytochrome oxidase, employing a more precise manometric technique. It also deals with the inhibition of succinic dehydrogenase, as was reported in a preliminary note (6), and records a similar effect upon lactic dehydrogenase; *d*-amino-acid oxidase, on the other hand, was only slightly inhibited.

Experimental

A. Inhibition of Catalase

Methods

Phenothiazone and phenothiazine sulphoxide were prepared by the methods of Pummerer and Gassner (17); the former was recrystallized from water, giving brick-red crystals melting at 165° C. (corr.); the sulphoxide was recrystallized from acetone. Leucophenothiazone was prepared by reduction of phenothiazone by Bernthsen's method (3).

---

[1] *Manuscript received in original form September 18, 1942, and as revised November 5, 1942.*
Contribution from the Institute of Parasitology, McGill University, Macdonald College, Que., with financial assistance from the National Research Council of Canada.

[2] *At the time, Lecturer, Institute of Parasitology, McGill University. At present, Assistant Professor of Biochemistry, Dalhousie University, Halifax, N.S.*

[3] *Research Assistant.*

A catalase extract was prepared from guinea-pig liver, as previously described (5). This extract was diluted 1 : 100 for use, and its activity was estimated manometrically in a Summerson differential manometer, at 15° C. The enzyme was made up to 1.0 ml. in buffer, $M/15$ in each of acetate and phosphate, pH 6.8; this was mixed with 0.3 ml. of 3% hydrogen peroxide at zero time. The control vessel contained substrate and buffer but no enzyme; under these conditions, the amount of decomposition in five minutes was virtually proportional to enzyme concentration. Inhibitors were dissolved in the buffer in each vessel, and were in contact with the enzyme during the 15 min. equilibration period.

Effect of Leucophenothiazone

This derivative was added as an alcoholic solution; the same volume of alcohol (never more than 0.1 ml.) was added to the standard enzyme, as it definitely stimulated catalase activity. The degree of inhibition thus observed is recorded in Table I; 50% inhibition requires about 6×10^{-6} M concentration of leucophenothiazone.

TABLE I

INHIBITION OF CATALASE BY LEUCOPHENOTHIAZONE

0.0003 ml. enzyme in 1.3 ml. total; pH 6.8, 15° C.

Inhibitor concentration, $M \times 10^6$	Oxygen liberated in five min., μl.	Inhibition, %
0	181	0
4	100	45
19	62	66
38	42	77

Effect of Phenothiazone

It was thought that the semiquinone form of phenothiazone might be the actual inhibitor. To test this hypothesis, phenothiazone was heated in glacial acetic acid or in 7 N hydrochloric acid, which converts a large proportion into the free radical form (see Granick, Michaelis, and Schubert (9)). This acid solution was then added to neutral acetate–phosphate buffer to give a resultant pH value of 5.3. No inhibition was observed, however, when catalase was added, and as previously noted (5) phenothiazone had no effect upon the enzyme at pH 7.

Effect of Sulphoxide

Phenothiazine sulphoxide was found to be a powerful inhibitor of catalase. For testing at pH 6.8 the compound was added in alcoholic solution, as in the case of leucophenothiazone. Table II gives the results of these tests, where it is seen that the point of 50% inhibition is at about 2.5×10^{-5} M concentration.

TABLE II

INHIBITION OF CATALASE BY SULPHOXIDE AT pH 6.8

0.0003 ml. enzyme in 1.3 ml. total volume; 15° C.

Sulphoxide concentration, $M \times 10^6$	Oxygen liberated in five min., μl.	Inhibition, %
0	232	0
0.8	197	15
7.7	156	33
26	113	51
77	97	58
230	44	81

The effect of increasing acidity upon the inhibition was also tested, in the hope of throwing light upon the possible role of the semiquinone form. The sulphoxide was dissolved by heating in 1 *N* hydrochloric acid, which gives the sulphonium chloride, according to Barnett and Smiles (1). This solution has a high concentration of the semiquinone of phenothiazine, as described by Michaelis, Granick, and Schubert (16). It was made up to contain varying concentrations of the sulphoxide and was added to the neutral acetate-phosphate buffer in sufficient volume to give a final pH value of 5.3. The inhibition of catalase, using these solutions, is shown in Table III; about 1×10^{-6} *M* concentration of sulphoxide is required to produce 50% inhibition.

TABLE III

INHIBITION OF CATALASE BY SULPHOXIDE AT pH 5.3

0.0010 ml. enzyme in 1.3 ml. total volume; 15° C.

Sulphoxide concentration, $M \times 10^7$	Oxygen liberated in five min., μl.	Inhibition, %
0	210	0
3	128	39
30	79	62
300	39	81

B. INHIBITION OF HEART MUSCLE ENZYMES

Methods

The preparation of phenothiazone and of its leuco form have already been described. Thionol was prepared by the original method of Bernthsen (3); the crude product was dissolved in sodium hydroxide and was precipitated by the addition of hydrochloric acid, giving an amorphous material melting at 134 to 136° C. (uncorr.). As noted by Granick, Michaelis, and Schubert (9), there is no satisfactory method for preparing pure thionol.

The enzyme was prepared from beef heart by the methods of Stotz and Hastings (18) and of Keilin and Hartree (12). Cytochrome-*c* was isolated from beef heart by the method of Keilin and Hartree (11).* Both types of enzyme preparation gave similar results, as far as the inhibitions were concerned. Cytochrome-*c*, added to 3×10^{-5} *M* concentration, increased the activity of the Keilin-Hartree enzyme, but did not affect that of the Stotz-Hastings preparation; nor did it affect the inhibitions observed. The Stotz-Hastings enzyme was used throughout in the experiments to be described—0.5 ml. of suspension in a total volume of 2.5 ml.

All measurements of enzyme activity were made manometrically, at 37° C. and at pH 7.3 in *M*/15 phosphate buffer; the control vessels contained enzyme but no substrate. Inhibitors were dissolved in the buffer, and were in contact with the enzyme during the 15 min. equilibration period, before mixing with substrate. Leucophenothiazone was most conveniently added by dissolving phenothiazone in the buffer, then reducing it with a little ascorbic acid. The same amount of ascorbic acid when added to the standard enzyme had no noticeable effect.

Succinoxidase Activity

The oxygen uptake of the total heart preparation was measured in the presence of 0.02 *M* succinate. Table IV indicates that the succinoxidase activity was slightly stimulated by low concentrations of phenothiazone and was strongly inhibited by higher concentrations. About 1.2×10^{-4} *M* phenothiazone gives a 50% decrease in oxygen consumption.

TABLE IV

INHIBITION OF HEART SUCCINOXIDASE BY PHENOTHIAZONE

0.5 ml. enzyme in 2.5 ml. total; pH 7.3, 37° C.

Phenothiazone concentration, $M \times 10^5$	Oxygen uptake in 60 min., µl.	Change in oxygen uptake, %
0	162	0
4	180	+ 11
8	107	− 34
16	61	− 62
50	0	−100

Thionol showed a much smaller inhibitory power. Under conditions similar to the above, the following results were obtained (oxygen consumption in 60 min.):—

Normal enzyme	128 µl.
Thionol, 0.001 *M*	101 µl.
Thionol, 0.003 *M*	32 µl.

---

* *In these preparations the Waring Blendor (Waring Corpn., 1697 Broadway, New York City) was found very useful for mincing tissue, to replace more tedious methods of grinding.*

Dehydrogenase Activity

The dehydrogenase activity of the heart preparation was measured in the presence of 0.02 *M* succinate, 0.002 *M* potassium cyanide, and 0.0004 *M* methylene blue. As seen in Table V, phenothiazone and thionol were strongly inhibitory, while leucophenothiazone had virtually no effect.

TABLE V

INHIBITION OF SUCCINIC DEHYDROGENASE

0.5 ml. enzyme in 2.5 ml. total; pH 7.3, 37° C.

Inhibitor	Concentration, *M*	O_2 uptake in 60 min., µl.		Decrease in O_2 uptake, %
		Normal	Treated	
Phenothiazone	0.0005	125	54	57
Leucophenothiazone	0.0005	110	96	13
Thionol	0.001	122	46	62

Cytochrome Oxidase Activity

The oxidase activity was determined in the presence of 0.01 *M p*-phenylenediamine. The results in Table VI indicate that phenothiazone had no effect; leucophenothiazone and thionol showed definite inhibitions.

TABLE VI

INHIBITION OF CYTOCHROME OXIDASE

0.5 ml. enzyme in 2.5 ml. total; pH 7.3, 37° C.

Inhibitor	Concentration, *M*	O_2 uptake in 30 min., µl.		Decrease in O_2 uptake, %
		Normal	Treated	
Phenothiazone	0.0005	176	178	0
Leucophenothiazone	0.00016	208	119	43
Thionol	0.003	248	194	22

C. OTHER ENZYME SYSTEMS

Inhibition of Lactic Dehydrogenase

A few preliminary experiments have been done with lactic dehydrogenase, prepared from yeast by treatment with acetone by Bernheim's method (2). A phosphate extract of the dried powder was tested on 0.2 *M dl*-lactate as substrate, in the presence of 5×10^{-4} *M* methylene blue, 0.2 *M* hydroxylamine, and a trace of boiled yeast extract. Phenothiazone, added to a concentration of 0.0005 *M*, was completely reduced to the leuco form. The results of a typical experiment were as follows (oxygen consumption in 60 min.):—

1.0 ml. yeast extract in 2.5 ml. volume	242 µl.
In presence of leucophenothiazone	137 µl.

Effect on d-Amino-acid Oxidase

This enzyme was prepared from pig kidney cortex by treatment with acetone according to Krebs (14). It was tested in phosphate buffer in the presence of 0.04 *M* *dl*-alanine. The activity was only slightly reduced by phenothiazone at 0.0005 *M* concentration, the normal oxygen consumption of 135 μl. in one hour being decreased to 110 μl. Leucophenothiazone in the same concentration had a negligible effect.

Effect on Urease

Because of the possibility of oxidation of free sulphydryl groups by phenothiazone, its effect upon urease was tested. Arlcourease was added to 2.5% urea in *M*/15 phosphate at pH 7.0, and the rate of decomposition was followed, at 37° C., by estimating the ammonia. The ammonia formed, as milli-equivalents per millilitre per hour, was as follows:—

No inhibitor	0.065 m.e.
Phenothiazone, 12×10^{-5} *M*	0.054 m.e.
Phenothiazone, 50×10^{-5} *M*	0.035 m.e.

It is therefore apparent that the dye, under these conditions, produces a partial inhibition of the enzyme activity.

Discussion

The inhibition of the enzymes catalase and cytochrome oxidase by leucophenothiazone has been confirmed by manometric methods. As previously suggested (5), this inhibition is attributed to the phenolic OH group, which probably forms covalent complexes with the active iron atoms of these haemin catalysts. (In the previous paper it was erroneously suggested that leucophenothiazone acts by combining with cytochrome, rather than with the oxidase, thus preventing reoxidation of the cytochrome.)

Phenothiazine sulphoxide has also been found to be a very powerful catalase inhibitor. Its activity at pH 5.3 is much greater than at pH 6.8, which suggests that the sulphonium ion is the active agent. Michaelis and his co-workers (9, 16) have discussed the strong resonance of the thiazine molecule, and this may be related to the enzyme inhibitions, but at present there is no evidence in favour of such a speculation.

In the case of the beef heart preparation it has been found that phenothiazone inhibits the succinoxidase activity (aerobic oxidation of succinate). On further analysis it was shown that the oxidized form of phenothiazone inhibits the dehydrogenase factor (i.e., that which is active in the presence of cyanide and methylene blue), while the leuco form of the dye inhibits the cytochrome oxidase activity.

Stotz and Hastings (18) correlated the inhibition of succinoxidase by dyes with the oxidation-reduction potentials of the dyes. Our results with phenothiazone correspond very closely with their findings. Thus, phenothiazone has an E_0' value of + 0.127 volts at pH 7.3, as interpolated from the data of

Granick, Michaelis, and Schubert (9)*; the degree of inhibition is similar to that in the presence of naphthosulphonate indophenol, with an E_0' value of + 0.105 volts. This suggests that phenothiazone acts upon the dehydrogenase by virtue of its relatively high oxidation–reduction potential, which is higher than that of the succinate–fumarate system or of cytochrome-*b*. The findings with urease suggest that the dye may have some effect upon the free SH groups of this enzyme, although it cannot be regarded as a very active oxidant for these groups.

Weil-Malherbe (19) and Keilin and Hartree (13) have observed an inhibition of heart succinoxidase by pyocyanin, which led to our experiments with phenothiazone. Keilin and Hartree proposed that pyocyanin may attack an intermediate link between the dehydrogenase and cytochrome oxidase; this may also be true of phenothiazone, where the over-all oxygen uptake is more strongly inhibited than is the dehydrogenase activity alone.

It is impossible at present to correlate these enzyme inhibitions, observed on mammalian tissue *in vitro*, with the anthelmintic, insecticidal, and bactericidal actions of the phenothiazine derivatives. It will be necessary to examine the effect of the compounds upon the enzyme systems of the actual organisms. Nevertheless, it may be of some significance that McIlwain (15) has proposed that anthelmintic drugs act as narcotics, and the observed inhibition of succinic and of lactic dehydrogenases fits in with Quastel's (10) well known theory of narcotic action.

References

1. BARNETT, E. DE B. and SMILES, S. J. Chem. Soc. 95 : 1253-1266. 1909.
2. BERNHEIM, F. Biochem. J. 22 : 1178-1192. 1928.
3. BERNTHSEN, A. Ann. 230 : 73-211. 1885.
4. COLLIER, H. B. Can. J. Research, D, 18 (7) : 272-278. 1940.
5. COLLIER, H. B. Can. J. Research, B, 18 (11) : 345-350. 1940.
6. COLLIER, H. B. and ALLEN, D. J. Biol. Chem. 140 (2) : 675-676. 1941.
7. COLLIER, H. B. and ALLEN, D. E. Can. J. Research, B, 20 (9) : 189-193. 1942.
8. DEEDS, F. and EDDY, C. W. J. Am. Chem. Soc. 60 (9) : 2079-2084. 1938.
9. GRANICK, S., MICHAELIS, L., and SCHUBERT, M. P. J. Am. Chem. Soc. 62 (7) : 1802-1810. 1940.
10. JOWETT, M. and QUASTEL, J. H. Biochem. J. 31 : 565-578. 1937.
11. KEILIN, D. and HARTREE, E. F. Proc. Roy. Soc. (London) B, 122 : 298-308. 1937.
12. KEILIN, D. and HARTREE, E. F. Proc. Roy. Soc. (London) B, 125 : 171-186. 1938.
13. KEILIN, D. and HARTREE, E. F. Proc. Roy. Soc. (London) B, 129 : 277-306. 1940.
14. KREBS, H. A. Biochem. J. 29 : 1620-1644. 1935.
15. McILWAIN, H. Lancet, 242 : 412-415. 1942.
16. MICHAELIS, L., GRANICK, S., and SCHUBERT, M. P. J. Am. Chem. Soc. 63 (2) : 351-355. 1941.
17. PUMMERER, R. and GASSNER, S. Ber. 46 : 2310-2327. 1913.
18. STOTZ, E. and HASTINGS, A. B. J. Biol. Chem. 118 (2) : 479-498. 1937.
19. WEIL-MALHERBE, H. Biochem. J. 31 : 299-312. 1937.

---

* *For thionol, E_0' is + 0.142 volts at pH 7.3, calculated from the data of DeEds and Eddy* (8).

SECTION B

INDEX TO VOLUME 20

Authors

Allen, D. E.—See Collier, H. B.

Anderson, G.—See Morris, A. C.

Baril, G. H., Barré, R., and Piché, L.—Contribution à l'étude des semicarbazides δ-substituées. III. Essai d'application au dosage du glucose, 33.

Barré, R.—See Baril, G. H.

Barré, R. and Piché, L.—Contribution à l'étude des semicarbazides δ-substituées. II. Semicarbazones de quelques aldéhydes et cétones, 17.

Basterfield, S. and Dyck, A. J.—Studies in urethanes. VII. Reactions of acyl diurethanes with ammonia and primary amines. Stabilizing effect of the phenyl radical in phenylmalonyl- and phenylsuccinyl-diurethane, 240.

Bois, E. and Chubb, W. O.—The sap of the birch tree, *Betula papyrifera* Marsh. I. The amylase system, 114.

Bois, E., Dugal, L. C., and Lessard, M.—Le calcium et le manganèse dans les sèves et les sirops d'érable, 1.

Bois, E. and Savary, J.—Les glucidases et les glucides d'*Ipomoea Batatas* et de *Solanum tuberosum*, 195.

Chapman, R. A. and McFarlane, W. D.—Pasture studies. XXIII. A proposed modification of the fluorimetric method for the estimation of riboflavin, 82.

Chubb, W. O.—See Bois, E.

Collier, H. B. and Allen, D. E.—Enzyme inhibition by derivatives of phenothiazine.
II. Inhibition of cholinesterase, 189.
III. Catalase, cytochrome oxidase, and dehydrogenases, 284.

Cuthbertson, A. C.—See McClure, J. H.

DeLong, W. A.—See MacDougall, D.

Dugal, L. C.—See Bois, E.

Dyck, A. J.—See Basterfield, S.

Eastcott, E. V. and Rae, J. J.—Factors in the culture medium that affect the phosphatase content of yeast, 202.

Evans, T. H., Levi, I., Hawkins, W. L., and Hibbert, H.—Studies on reactions relating to carbohydrates and polysaccharides. LXVII. Synthesis of methylated glucose derivatives, 175.

Graham, G. T. E. and Thorvaldson, T.—The removal of copper and cadmium in the hydrometallurgy of zinc, 93.

Greey, P. H.—See Marchant, C.

Hawkins, W. L.—See Evans, T. H.

Hendrickson, L., Hutcheon, A. T., and Spinks, J. W. T.—Aromatics in Turner Valley crudes, 231.

Hibbert, H.—See Evans, T. H.

Hopkins, C. Y.—Taste differences in compounds having the NCS linkage, 268.

Hutcheon, A. T.—See Hendrickson, L.

Kenalty, B. J.—See White, W. H.

Leger, F.—See Manske, R. H. F.

Lessard, M.—See Bois, E.

Levi, I.—See Evans, T. H.

Lucas, C. C.—See Marchant, C.

McClelland, L.—See Marchant, C.

McClure, J. H., Robertson, R. E., and Cuthbertson, A. C.—The decomposition of benzoyl peroxide in benzene, 103.

MacDougall, D. and DeLong, W. A.—Effect of initial drying temperature on the apparent lignin content of plant tissues, 40.

McFarlane, W. D.—See Chapman, R. A.

McLean, J. D., Rabinovitch, B. S., and Winkler, C. A.—The hydrolysis of propionitrile in concentrated solutions of mineral acids, 168.

Manske, R. H. F.—
- The alkaloids of Fumariaceous plants
  - XXXI. *Corydalis montana* (Engelm.) Britton, 49.
  - XXXIII. *Corydalis Cheilantheifolia* Hemsl., 57.
- The alkaloids of Papaveraceous plants
  - XXXII. *Stylophorum diphyllum* (Michx). Nutt., *Dicranostigma franchetianum* (Prain) Fedde, and *Glaucium serpieri* Heldr., 53.
- The natural occurrence of 3-methoxy-pyridine, 265.

Manske, R. H. F.—See Marion, L.

Manske, R. H. F. and Marion, L.—The alkaloids of *Lycopodium* species. I. *Lycopodium complanatum* L., 87.

Manske, R. H. F., Marion, L., and Leger, F.—The synthesis and the characterization of the monomethyl- and the dimethyl-quinolines, 133.

Marchant, C.—The identification of Bios V as vitamin B_1 and of a constituent of Bios VII solution as vitamin B_6; their effect upon the reproduction of *Saccharomyces hanseniaspora valbyensis*, Yeast 2335, and *Saccharomyces galactosus*, 21.

Marchant, C., Lucas, C. C., and McClelland, L.—Chemotherapeutic studies: preparation of substituted sulphonamides—with an appendix—The determination of chemotherapeutic activity—by **P. H. Greey,** 5.

Marion, L.—The isolation of cicutin from *Cicuta maculata* L., 157.

Marion, L.—See Manske, R. H. F.

Marion, L. and Manske, R. H. F.—The alkaloids of *Lycopodium* species. II. Some degradation experiments with lycopodine, 153.

Monteith, G. E.—See Munro, L. A.

Morris, A. C., Munn, L. T., and Anderson, G.—The system ethanol–methanol at 40° C., 207.

Munn, L. T.—See Morris, A. C.

Munro, L. A., and Monteith, G. E.—The syneresis of silica gels containing addition agents, 212.

Pett, L. B.—See Waagen, H. K.

Piché, L.—See Baril, G. H., Barré, R.

Rabinovitch, B. S.—See McLean, J. D.

Rabinovitch, B. S. and Winkler, C. A.—
Note on the pyrolysis of methyl and ethyl cyanides, 69.
The hydrolysis of acid amides in concentrated hydrochloric acid solutions, 73.
Kinetics of the alkaline hydrolysis of propionitrile, 185.
The hydrolysis of aliphatic nitriles in concentrated hydrochloric acid solutions, 221.

Rabinovitch, B. S., Winkler, C. A., and Stewart, A. R. P.—The hydrolysis of propionitrile in concentrated hydrochloric acid solutions, 121.

Rae, J. J.—See Eastcott, E. V.

Robertson, R. E.—See McClure, J. H.

Savary, J.—See Bois, E.

Spinks, J. W. T.—See Hendrickson, L.

Stewart, A. R. P.—See Rabinovitch, B. S.

Taylor, E. G.—Studies on dicyanotrizaole. I. The conductance of dilute aqueous solutions of dicyanotriazole at 25° C., 161.

Thode, H. G. and Walkling, F. O.—Column packing and the separation of isotopes, 61.

Thorvaldson, T.—See Graham, G. T. E.

Waagen, H. K. and Pett, L. B.—The adequacy of vitamin C in Alberta diets, 246.
Some sources of vitamin C in Alberta, 274.

Walkling, F. O.—See Thode, H. G.

White, W. H., Winkler, C. A., and Kenalty, B. J.—The reaction of hydrogen atoms with isobutane, 255.

Winkler, C. A.—See McLean, J. D., Rabinovitch, B. S., White, W. H.

SECTION B

INDEX TO VOLUME 20

Subjects

Acetamide
  Hydrolysis of, in concentrated hydrochloric acid solutions, 73.
  Thio-, Taste tests with, 270.

Acetanilide, Thio-, Taste tests with, 270.

Acetic acid, Cyano-, Hydrolysis of, in concentrated hydrochloric acid solutions, 221.

Acetone semicarbazones, as agents for determination of acetone, 18, 19.

Acetonitrile
  Hydrolysis of, in concentrated hydrochloric acid solutions, 221.
  Pyrolysis of, 69.

Acid amides, Hydrolysis of, in concentrated hydrochloric acid solutions, 73.

Acriflavine, Inhibition of cholinesterase by, 192.

Acyl diurethanes, Reactions of, with ammonia and primary amines, 240.

Alberta diets, Vitamin C in,
  Adequacy of, 246.
  Sources of, 274.

Alcohols, Effect of, on syneresis of silica gels, 212.

Aliphatic nitriles, See Nitriles, Aliphatic.

Alkaline hydrolysis of propionitrile, Kinetics of, 185.

Alkaloid 56 from Corydalis montana, 49.

Alkaloid F57 from Corydalis montana and C. aurea, 49.

Alkaloids L1, L2, L3, L4, L5, and L6 from Lycopodium complanatum, 87, 90, 91.

Alkaloids of fumariaceous plants,
  XXXI. Corydalis montana (Engelm.) Britton, 49.
  XXXIII. Corydalis Cheilantheifolia Hemsl., 57.

Alkaloids of lycopodium species
  I. Lycopodium complanatum L., 87.
  II. Some degradation experiments with lycopodine, 153.

Alkaloids of papaveraceous plants,
  XXXII. Stylophorum diphyllum (Michx.) Nutt., Dicranostigma franchetianum (Prain) Fedde, and Glaucium serpieri Heldr., 53.

Allocryptopine from Corydalis Cheilantheifolia, 57.

Amides, Acid, Hydrolysis of, in concentrated hydrochloric acid solutions, 73.

Amines, Primary, See Aniline, Ethylamine.

***d*-Amino-acid oxidase**, See under Enzyme inhibition.

Ammonia, Reactions of, with phenylmalonyl- and phenylsuccinyl-diurethane, 243, 244.

Amylase system in sap of birch tree, 114.

Analysis, A proposed modification of the fluorimetric method for the determination of riboflavin, 82.

Aniline, Reactions of, with phenylmalonyl- and phenylsuccinyl-diurethane, 243, 244.

Aromatics in Turner Valley crudes, Determination of, by specific dispersion method—benzene, toluene, xylenes, 231.

Ascorbic acid, See Vitamin C in Alberta diets.

Aurotensine from Glaucium serpieri, 53.

Bacteriostatic activity of substituted sulphonamides, Determination of, 5, 13.

Barbituric acid, Thio-, Taste tests with, 270.

Benzaldehyde, *p*-Nitrophenyl-4-semicarbazone of, Melting point of, 19.

Benzamide, Hydrolysis of, in concentrated hydrochloric acid solutions, 73.

Benzene
  Decomposition of benzoyl peroxide in, 103.
  See under Aromatics.

Benzenesulphonyl chloride, *p*-Acetylamino-, 7.
  Condensation with amines, 6.

Benzidene, Bis-(acetyl-sulphanilyl)- and bis-(sulphanilyl)-, 5.

Benzoyl peroxide, Decomposition of, in benzene, 103.

Berberine from Corydalis Cheilantheifolia, 58.

Betula papyrifera (birch tree), Sap of, The amylase system of, 114.

Bios IIB, Crude, Fractionation of, into purified Bios IIB and Bios VII, 27.

Bios V, Identification of, as vitamin B_1, and of a constituent of Bios VII solution as vitamin B_6; their effect on the reproduction of Saccharomyces hanseniaspora valbyensis, Yeast 2335, and S. galactosus, 21.

Bios VII solution, Identification of a constituent of, as vitamin B_6, 21, 29.
  Effect on reproduction of yeasts, 21.
  Fractionation of crude Bios IIB into purified Bios IIB and, 27.

Bios VIII, Experiments with, 31.

Birch tree, Sap of, The amylase system of, 114.

Buffers, Effect of buffering of the growth medium on the phosphatase content of yeast, 202.

Cadmium and copper, Removal of, in the hydrometallurgy of zinc, 93.

Calcium in maple saps and sugars, 1.

***l*-Canadine** from Corydalis Cheilantheifolia, 57.

Capauridine from Corydalis montana, 49.

Capaurimine from Corydalis montana, 49.

Capaurine from Corydalis montana, 49.

Carbohydrates and polysaccharides, Studies on reactions relating to, LXVII. Synthesis of methylated glucose derivatives, 175.

Catalase, See under Enzyme inhibition.

Cellobiogenic amylase in birch sap, 114.

Cellobiose in birch sap, 114.

***l*-Cheilanthifoline** from Corydalis Cheilantheifolia, 57.

Chelidonine from Stylophorum diphyllum and Dicranostigma franchetianum, 53.

Chemical exchange, Comparison of various types of column packing on, 66.

Chemotherapeutic activity, Determination of, 13.

Chemotherapy, Studies in, Preparation of substituted sulphonamides, 5.

Cholinesterase, See under Enzyme inhibition.

Cicuta maculata, Isolation of cicutin from, 157.

Cicutin
  Hydrolytic methylation of, 160.
  Isolation of, from Cicuta maculata, 157.

Column packing(s)
  and chemical exchange, 66.
  Comparison of, in distillation of hydrocarbons and of water systems, 63.
  and the separation of isotopes, 61.

Complanatine, (L1), an alkaloid from Lycopodium complanatum, 87, 89.

Conductance of dilute aqueous solutions of dicyanotriazole at 25° C., 161.

Copper, Removal of, in the hydrometallurgy of zinc, 93.

Corydaline from Corydalis montana, 49.

Corydalis aurea, Alkaloid F57 from, 49.

Corydalis Cheilantheifolia, Alkaloids from, 57.

***l*-Corypalmine** from Corydalis Cheilantheifolia, 57.

Culture media, Factors in, that affect the phosphatase content of yeast, 202.

Cyclohexylamine, Reaction of, with malonyl-diurethane, 245.

Cytochrome oxidase, See under Enzyme inhibition.

Dehydrogenase, See Succinic and Yeast lactic dehydrogenases under Enzyme inhibition.

Dehydrogenation of lycopodine with selenium, 153.

Dicranostigma franchetianum, Alkaloids from, 53.

Diets, Alberta, See Alberta diets.

Dispersion method for determination of aromatics in presence of paraffinic and naphthenic hydrocarbons, 231.

Distillation
  Column packing and the separation of isotopes, 61.
  Comparison of types of column packing, 63.
  on chemical exchange, 66.

Drying of plant tissues,
  Effect of initial drying temperature on apparent lignin content of, 40.

- **Enzyme inhibition** by phenothiazine derivatives, 284.
  - *d*-Amino-acid oxidase by phenothiazone, 289.
  - Catalase by
    - leucophenothiazone, 285.
    - phenothiazine sulphoxide, 285.
  - Cholinesterase by
    - acriflavine, 192.
    - eserine, 192.
    - methylene blue, 191.
    - phenothiazine methyl-sulphonium perchlorate, 191.
    - phenothiazone, 191.
  - Cytochrome oxidase by leucophenothiazone and thionol, 288.
  - Succinic dehydrogenase by oxidized form of phenothiazone, 284.
  - Succinic oxidase by
    - phenothiazone, 287.
    - thionol, 287.
  - Urease and yeast lactic dehydrogenase by phenothiazonc, 289.
- **Enzymes**
  - Glucidases in Ipomoea Batatas and Solanum tuberosum, 195.
- **Equisetum arvense,** 3-Methoxy-pyridine from, 366.
- **Erythritol** Effect of, on syneresis of silica gels, 212.
- **Eserine,** Inhibition of cholinesterase by, 190.
- **Ethanol–methanol system,** at 40° C., 207.
- **Ethyl alcohol**
  - Effect of, on syneresis of silica gels, 212.
  - See Ethanol.
- **Ethylamine,** Reactions of, with phenylmalonyl- and phenylsuccinyl- diurethane, 243, 244.
- **Ethyl cyanide,** Pyrolysis of, Note on, 69.
- **Fluorimetric method** for the estimation of riboflavin, proposed modification of, 82.
- **Foodstuffs,** A proposed modification of the fluorimetric method for the estimation of riboflavin in, 82.
- **Formamide,** Hydrolysis of, in concentrated hydrochloric acid solutions, 73.
- **Fractionating columns,** Study of an expanded shale aggregate packing material for, 61.
- **Fumariaceous plants,** Alkaloids of, 49, 57.
- **Fungi**
  - Yeast(s)
    - Factors in culture medium that affect the phosphatase content of, 202.
    - See under Bios V.
- **Gels,** Silica, containing addition agents, syneresis of, 212.
- **Glaucine** from Glaucium serpieri, 53.
- **Glaucium serpieri,** Alkaloids from, 53.
- **Glucidases** of Ipomoea Batatas and Solanum tuberosum, 195.
- **Glucides** of Ipomoea Batatas and Solanum tuberosum, 195.
- **Glucogenic amylase** in birch sap, 114.
- **Gluconic acid, 2,3 -Dimethyl-,** 179.
- **Gluconophenylhydrazide, 2,3- Dimethyl-,** 179.
- **Glucose**
  - Application of *p*-nitrophenyl-4-semicarbazide to determination of, 33.
  - derivatives, Methylated, 175.
  - in sap of birch tree, 114.
  - semicarbazones as agents for the determination of glucose, 18, 19.
- **Glucose**
  - 2, 3-Dimethyl-, 175, 181.
  - 2, 3, 4, 6-Tetramethyl-, 175, 182.
  - Tribenzoyl-2, 3-dimethyl-, 181.
  - 2, 3, 4-Trimethyl-, 175, 182.
- **Glucoside(s)**
  - 4,6-Benzylidene-α- and β-methyl, 178, 180.
  - Dibenzoyl-2,3-dimethyl-β-methyl, 181.
  - 2,3-Dimethyl-4,6-benzylidene-α- and β-methyl, 178, 180.
  - 2,3-Dimethyl-α- and β-methyl-, 178, 180.
  - Tetra-acetyl-β-methyl, 176, 180.
  - 2,3,4,6-Tetramethyl-α-methyl, 182.
  - 2,3,4-Trimethyl-α- and β-methyl, 175, 182.
- **Glycerol,** Effect of, on syneresis of silica gels, 212.
- **Glycol,** Effect of, on syneresis of silica gels, 212.
- **Glyoxylic acid,** *p*-Nitrophenyl-4-semicarbazone of, Melting point, 19.
- **Hydrobromic acid,** Concentrated, Hydrolysis of propionitrile in, 168.

Hydrocarbons
- Distillation of, in a column containing expanded shale aggregate packing, 61.
- Paraffinic and naphthenic, Dispersion method for determination of aromatics in presence of, 231.
- See also under names of individual hydrocarbons.

Hydrochloric acid solutions, concentrated,
- Hydrolysis in, of
  - acid amides, 73.
  - aliphatic nitriles, 221.
  - propionitrile, 121.

Hydrocyanic acid, Hydrolysis of, in concentrated hydrochloric acid solutions, 221.

Hydrogen atoms, Reaction of, with isobutane, 255.

Hydrogen ion concentration,
- Effect of, in precipitation of copper and cadmium in hydrometallurgy of zinc, 93.
- of growth medium, Effect of, on phosphatase content of yeast, 203.
- and syneresis of silica gels containing addition agents, Relation of, 217.

Hydrolysis of
- N^4-acetyl-N^1-substituted sulphanilamides, 5.
- acid amides in concentrated hydrochloric acid solutions, 73.
- aliphatic nitriles in concentrated hydrochloric acid solutions, 221.
- propronitrile in concentrated mineral acids, 121, 168; in sodium hydroxide, 185.
- starch; by birch sap, 115; by juice of Ipomoea Batatas and Solanum tuberosum, 195.

Hydrometallurgy of zinc, Removal of copper and cadmium in, 93.

Inhibition of cholinesterase by derivatives of phenothiazine, 189.

Ipomoea Batatas, Glucidases and glucides of, 195.

Isobutane, Reaction of hydrogen atoms with, 255.

Isocorydine from Glaucium serpieri, 53.

Isodithiocyanic acid, Taste tests with, 270.

Isotopes, Column packing and the separation of, 61.

Kinetics of
- alkaline hydrolysis of propionitrile, 185.
- decomposition of benzoyl peroxide in benzene, 103.
- See under Hydrolysis.

Lactic dehydrogenase, Yeast, See under Enzyme inhibition.

Lepidine, Preparation of, 149.

Levoglucosan, 2, 3, 4-Trimethyl-, 181.

Lignin content of plant tissues, Apparent, Effect of initial drying temperature on, 40.

Lycopodine
- degradation with selenium, 154.
- dehydrogenation of, with palladium, 155.
- Isolation of 7-methyl- and 5 : 7-dimethylquinoline from, 154.
- from lycopodium complanatum, 87.
- Reaction with phthalic anhydride, 155.

Lycopodium species, Alkaloids of, 87, 153.

Magnesium in growth medium, Effect of, on phosphatase content of yeast, 204, 205.

Manganese in maple saps and sugars, 1.

Maple saps and sugars, Calcium and manganese in, 1.

Metallurgy, Hydro-, of zinc, Removal of copper and cadmium in, 93.

Methanol-ethanol system at 40°C., 207.

Methyl alcohol
- Effect of, on syneresis of silica gels, 212.
- See Methanol.

Methyl cyanide, Pyrolysis of, Note on. 69.

Methylene blue, Inhibition of cholinesterase by, 191.

NCS linkage, Taste differences in compounds having the, 268.

Nicotine from
- Equisetum arvense, 87, 92.
- Lycopodium complanatum, 87, 92.

Nitric acid, Concentrated, Hydrolysis of propionitrile in, 168.

Nitriles, Aliphatic, Hydrolysis of, in concentrated hydrochloric acid solutions, 221.

***m*-Nitrobenzaldehyde,** *p*-Nitrophenyl-4-semicarbazone of, Melting point, 19.

Nitrogen–carbon–sulphur linkage, Taste differences in compounds having the, 268.

Nutrition
- Adequacy of vitamin C in Alberta diets, 246.
- Some sources of vitamin C in Alberta, 274.

Obscurine, (L6), an alkaloid from Lycopodium complanatum, 87, 91.

Ophiocarpine, Oxidation of, 60.

Oxazolidine derivatives, Taste tests with, 268.
- 2-Thion-4, 4-dimethyl-, 269.
  - Preparation, 273.
- 2-Thion-5, 5-dimethyl-, 269.
- 2-Thion-5-methyl-, 269.
  - Preparation, 272.

Oxidase, See *d*-Amino-acid, cytochrome, and succinic oxidases under Enzyme inhibition.

Oxidation of ophiocarpine, 60.

Packing, Column, See Column packing.

Palladium, Dehydrogenation of lycopodine with, 155.

Palmatine, Tetrahydro-*dl*- from Corydalis montana, 49.

Papaveraceous plants, Alkaloids of, 53.

Pasture studies
- XXIII. A proposed modification of the fluorimetric method for the estimation of riboflavin, 82.

Petroleum, Aromatics in Turner Valley crudes, determination of, by specific dispersion method, 231.

Phenothiazine derivatives, Enzyme inhibition by
- II. Inhibition of cholinesterase, 189.
- III. Catalase, cytochrome oxidase, and dehydrogenases, 284.
- See under Enzyme inhibition.

***p*-Phenylene-diamine, Bis-(acetyl-sulphanilyl)-** and **bis-(sulphanilyl)-,** 5.

Phenyl radical, Stabilizing effect of, in phenylmalonyl- and phenyl-succinyl-diurethane, 240.

Phosphatase content of yeast, Factors in the culture medium that affect the, 202.

Phosphate in growth medium, Effect of, on phosphatase content of yeast, 204, 205.

Phthalic anhydride, Reaction with lycopodine, 155.

Physostigmine, See Eserine.

Plant tissues, Effect of initial drying temperature on the apparent lignin content of, 40.

Polysaccharides, Studies on carbohydrates and, 175.

Potato, See Ipomoea Batatas and Solanum tuberosum.

Pressure(s) Total and partial, of system ethanol–methanol at 40° C., 209.

Propane, 2-Methyl-, Reaction of hydrogen atoms with, 255.

Propene, γ,γ,γ-Trichloro-α-(3-methyl-4-quinolyl)-, 145.

Propionamide, Hydrolysis of, in concentrated hydrochloric acid solutions, 73.

Propionitrile, Hydrolysis of,
- in concentrated solutions of hydrochloric acid, 121.
- in hydrobromic, nitric, and sulphuric acids, 168.
- Kinetics of alkaline, 185.

Protopine from
- Corydalis Cheilantheifolia, 57.
- Corydalis montana, 49.
- Dicranostigma franchetianum, 53.
- Glaucium serpieri, 53.
- Stylophorum diphyllum, 53.

Pyridine, 3-Methoxy-,
- from Thermopsis rhombifolia and Equisetum arvense, 265.
- Synthesis, 267.

Pyrolysis of methyl and ethyl cyanides, Note on, 69.

Pyruvic acid, *p*-Nitrophenyl-4-semicarbazone of, Melting point, 19.

Quinaldine, 142.

Quinoline
- 8-amino-2 : 5-dimethyl-, 143.
- 8-amino-3 : 5-dimethyl-, 146.
- 8-amino-4 : 5-dimethyl-, 151.
- 8-amino-5 : 6-dimethyl-, 141.
- 8-amino-5-methyl-, 139.
- 2 : 3-, 2 : 4-dimethyl-, 144; 2 : 5-dimethyl-, 142; 2 : 6-, 2 : 7-, 2 : 8-dimethyl-, 143.
- 3 : 4-dimethyl-, 145; 3 : 5-, 3 : 6-, 3 :7-dimethyl, 146; 3 : 8-dimethyl-, 148.
- 4 : 5-, 4 : 6-, 4 : 7-, 4 : 8-dimethyl-, 150.
- 5 : 6-dimethyl-, 142.
- 5 : 7-dimethyl-, 140.
  - production in degradation of lycopodine, 154.
- 5 : 8-dimethyl-, 140.
- 6 : 7-dimethyl-, 141; 6 : 8-dimethyl-, 142.
- 7 : 8-dimethyl-, 142.
- 7-ethyl-, 139.

Quinoline—*concluded*
  2-hydroxy-8-methoxy-4 : 5-dimethyl-, 150.
  2-methyl-, 142.
  3-methyl-, 144.
  4-methyl-, 149.
  5-methyl-, 139.
  6-methyl-, 140.
  7-methyl-, 140.
    production in degradation of lycopodine, 154.
  8-methyl-, 140.
  3-methyl-6-bromo-, 149.
  8-nitro-2 : 5-dimethyl-, 143.
  8-nitro-3 : 5-dimethyl-, 145.
  8-nitro-4 : 5-dimethyl-, 151.
  8-nitro-5 : 6-dimethyl-, 141.
  8-nitro-5-methyl-, 139.
  2 : 3 : 6-, 2 : 3 : 8-trimethyl-, 144.
  3 : 4 : 7-trimethyl-, 148.
  See also Propene, γ-γ-γ-Trichloro-α-(3-methyl-4-quinolyl)-.

Quinolines, Preparation and characterization of monomethyl- and dimethyl-, 133.

Reaction kinetics
  of the hydrolysis of
    acid amides in concentrated hydrochloric acid, 73.
    aliphatic amines in concentrated hydrochloric acid, 221.
    propionitrile in concentrated mineral acids, 168, 121.
  of reaction of hydrogen atoms with isobutane.
  See also Kinetics.

Refractive Index, Specific dispersion method for determination of aromatics in presence of paraffinic and naphthenic hydrocarbons, 231.

Riboflavin, Estimation of, A proposed modification for the, 82.

Saccharomyces galactosus, See under Bios V.

Saccharomyces hanseniaspora valbyensis, See under Bios V.

Sap
  of birch tree. I. The amylase system, 114.
  Maple, and syrup, Calcium and magnesium in, 1.

Scoulerine from Corydalis montana, 49.

Selenium, Dehydrogenation of lycopodine with, 153.

Semicarbazides, δ-Substituted, Contribution to the study of,
  II. Semicarbazones of some aldehydes and ketones, 17.
  III. Application to determination of glucose, 33.

Semicarbazide(s), δ-Substituted, as agents for identification and determination of aldehydes and ketones (acetone and glucose), 17.
    Benzyl-4-, 17.
    p-Bromophenyl-4-, 17.
    o, *p*-Dinitrophenyl-4-, 17.
    Diphenyl-4-4-, 17.
    p-Nitrophenyl-4-, 17.
      application to determination of glucose, 33.
    p-Nitroxenyl-4-, 17.
    Phenyl-4-, 17.
    Xanthyl-4-, 17.
    p-Xenyl-4-, 17.

Semicarbazones, as agents for determination of aldehydes and ketones, 18, 19, 33.
  See also Semicarbazides.

Shale aggregate packing
  Analysis of, 62.
  for fractionating columns, 61.

Silica gels containing addition agents, Syneresis of, 212.

Sodium hydroxide, Kinetics of hydrolysis of propionitrile in, 185.

Solanum tuberosum, Glucidases and glucides of, 195.

Specific dispersion method for determining aromatics in presence of paraffinic and naphthenic hydrocarbons, 231.

Starch, Hydrolysis of,
  by birch sap, 115.
  by juice of Ipomoea Batatas and Solanum tuberosum, 195.

Stylophorum diphyllum, Alkaloids from, 53.

Stylopine from
  Corydalis Cheilantheifolia, 58.
  Dicranostigma franchetianum, 55.
  Stylophorum diphyllum, 55.

Succinic dehydrogenase and oxidase, See under Enzyme inhibition.

Sulphanilamides, Substituted, 5.

Sulphanilamide(s)
  N^4-acetyl-N^1-substituted, 5.
  N^1-substituted, 5.
    N^1-(4-acetylphenyl), 5.
    N^1-(2-aminophenyl), 5, 12.
    N^1-(3-aminophenyl), 5.
    N^1-(4-aminophenyl), 5.
    N^1-(4-arsonophenyl), 5.
    N^1-(4-benzoylphenyl), 5.
    N^1-(4-bromophenyl), 5.
    N^1-(2-carbethoxyphenyl), 5.
    N^1-(3-carbethoxyphenyl), 5.
    N^1-(4-carbethoxyphenyl), 5.
    N^1-(2-carboxyphenyl), 5.
    N^1-(3-carboxyphenyl), 5.
    N^1-(4-carboxyphenyl), 5, 10.
    N^1-(2, 4-dimethylphenyl), 5.
    N^1-(2, 6-dimethylphenyl), 5.
    N^1-(β-hydroxyethyl), 5.
    N^1-(4-methoxy-2-aminophenyl), 5.
    N^1-(6-methoxy-3-aminophenyl), 5, 11.
    N^1-(2-methoxy-5-methylphenyl), 5.
    N^1-(4-methoxy-2-nitrophenyl), 5.
    N^1-(6-methoxy-3-nitrophenyl), 5.
    N^1-(2-methoxyphenyl), 5.
    N^1-(3-methoxyphenyl), 5.
    N^1-(4-methoxyphenyl), 5, 9.
    N^1-(4-methyl-3-aminophenyl), 5.
    N^1-(6-methyl-3-aminophenyl), 5.
    N^1-(2-methyl-5-isopropylphenyl), 5.
    N^1-(4-methyl-3-nitrophenyl), 5.
    N^1-(6-methyl-3-nitrophenyl), 5.
    N^1-(2-methylphenyl), 5.
    N^1-(3-methylphenyl), 5.
    N^1-(4-methylphenyl), 5.
    N^1-(2-nitrophenyl), 5.
    N^1-(3-nitrophenyl), 5.
    N^1-(4-nitrophenyl), 5.

Sulphur compounds, Taste tests with, 268.

Sulphuric acid, Concentrated, Hydrolysis of propionitrile in, 168.

Syneresis of silica gels containing addition agents, 212.

System ethanol-methanol at 40° C., 207.

Taste differences in compounds having the NCS linkage, 268.

Temperature,
  Initial drying, effect of, on apparent lignin content of plant tissues, 40.

Thermopsis rhombifolia, 3-Methoxy-pyridine from, 266.

Thiazine methyl sulphonium ion, Inhibition of cholinesterase by, 192.

Thiazolidine derivatives, taste tests with,
  2-Thion-, 269.
  2-Thion-5, 5-dimethyl-, 269.
  2-Thion-5-methyl-, 269.
    Preparation, 272.

Thiazoline derivatives, Preparation and taste tests with,
  2-Oxo-4, 5-dimethyl-, 269, 272.
  2-Oxo-4-methyl-, 269, 273.
  2-Oxo-4-methyl-5-bromo-, 269.
  2-Thion-4, 5-dimethyl-, 269, 272.

Toluene, See under Aromatics.

***p*-Toluylene-diamine, Bis-(acetyl-sulphanilyl)-** and **bis-(sulphanilyl)-,** 5, 11.

Triazole, Dicyano-, Studies on,
  I. The conductance of dilute aqueous solutions of dicyanotriazole, at 25° C., 161.

Turner Valley crudes, Aromatics in, Determination of, by dispersion method—
    benzene, toluene, xylenes, 231.

Urea, Allylthio- and **phenylthio-,**
  Taste tests with, 270.

Urease, See under Enzyme inhibition.

Urethanes, Studies in,
  VII. Reactions of acyl diurethanes with ammonia and primary amines. Stabilizing effect of the phenyl radical in phenylmalonyl- and phenylsuccinyl-diurethane, 240.

Urethane(s) Di-,
  Malonyl-, Reaction of, with cyclohexylamine, 245.
  Phenylmalonyl- and phenylsuccinyl-, Reactions with ammonia, aniline, and ethylamine, 240.

Vanillin, *p*-Nitrophenyl-4-semicarbazone of, melting point, 19.

Vitamin B_1, See under Bios V.

Vitamin B_6, See under Bios VII.

Vitamin C in Alberta diets
  Adequacy of, 246.
  Sources of, 274.

Water systems, Distillation of, in a column containing an expanded shale aggregate packing material, 61.

Xylenes, See under Aromatics.

Yeast(s), See Fungi, and under Enzyme inhibition.

Zinc, Removal of copper and cadmium in the hydrometallurgy of, 93.

ERRATUM

Page 246, line 1 of footnote 1, for "August 28" read "August 3".